Electrical, thermomechanical and sorption properties of hybrid organic-inorganic systems based on urethane oligomers and silicates

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Propriétés électriques, thermomécaniques et de sorption de systèmes hybrides organique-inorganique basés sur des oligomères uréthanes et silicates

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General Introduction

Urgency of the topic. Hybrid organic-inorganic systems (OIS) are a new class of polymer materials, high interest to which appeared in recent years. It is explained by their peculiar structure, which includes organic and inorganic units, and, accordingly, possesses their common properties. Such combination provides the opportunity to obtain materials with predefined properties, which are regulated by variation of chemical composition of organic and inorganic components. Considering onrush of up-to-date technology, that require new materials with specific properties, their application area is constantly expanding. Overall, it is often that new hybrid organic-inorganic polymer systems show characteristics, which far exceed the corresponding characteristics of the existing analogs (for example, well known solid polymer electrolyte Nafion compared to traditional electrolyte).

However, the synthesis of hybrid organic-inorganic polymer systems is usually sequential and technologically complex process, that inhibits the widespread use of such systems. Work carried out in Institute of Macromolecular Chemistry of National Academy of Science of Ukraine showed the possibility of synthesis of hybrid organic-inorganic systems by reactions of organic and inorganic oligomers that contain reactive groups. This method of OIS obtaining is very attractive from a technological point of view. One of such promising hybrid systems is OIS based on urethane oligomers and metal silicate, in which polymerization occurs due to reactions between free reactive NCO-groups of the organic component and OH-groups of the inorganic component. However, in spite of the presence of many R-efforts, that focus on the progress of chemical reactions in these OIS, physicochemical properties of hybrid systems and their relationships with the structure are not sufficiently investigated. Therefore, the study of a wide range of properties (mechanical, thermal, electrical and sorption) of this type of OIS, whose structure and, consequently, properties are changed in a wide range, establishing the relationship between them and creating models, that would explain patterns found, are especially urgent.

Links with scientific programs, plans, themes. This research was performed in the department of polymer composites of Institute of Macromolecular Chemistry of National Academy of Sciences of Ukraine according to the scientific planes of the institute under the government's themes: 2004-2008 2.1.11.5-9 (№0104U000071) «Synthesis and investigations of polymer nanohybrid networks, which include inorganic units»; 2007-

2011. 2.1.11.5-10 (№0106U010376) «The development of chemistry and physicochemistry of functional polymers and polymer systems». Part of the thesis was also done in Laboratory of polymer materials and biomaterials of University Claude Bernard Lyon 1, CNRS, France according «Agreement for international joint supervision of a thesis" between Institute of Macromolecular Chemistry of NAS and University Claude Bernard Lyon 1, CNRS, France in the framework of international scientific cooperation between Institute of Macromolecular Chemistry of NAS of Ukraine and Laboratory of Polymer Materials and Biomaterials of University Claude Bernard Lyon 1, CNRS, France and with the concurrence of Higher Accreditation Commission of Ukraine № 95/19-1-11-61 on 31.01.08.

The purpose and tasks of the research. The aim of the research is to establish mechanisms of structure formation of hybrid organic-inorganic systems based on urethane oligomers and silicates, depending on reactivity of organic component, to identify the impact of structural organization of OIS obtained on their electrophysical and thermomechanical properties, sorption and sensory activity.

Realization of this aim supposed to solve the following ***tasks***:

- study of the formation of OIS structure depending on the concentration of free reactive NCO- groups in the organic component;
- study of the thermomechanical behavior of OIS depending on their structure;
- investigation of electrical and dielectric properties of OIS depending on the compounds ratio of organic component in the wide frequency and temperature ranges;
- study of the influence of composition of organic component on sorption activity and sensitivity of hybrid systems;
- creating a spatial structural model and a model of conductivity of organic-inorganic hybrid polymer systems.

The object of the research is a mechanism of formation of hybrid organic-inorganic polymer systems and the impact of structural organization of OIS formed on their properties.

The subject of the research is the process of structure formation of hybrid organic-inorganic systems based on macrodiisocyantae, polyisocyanate (organic components) and

sodium silicate (inorganic component), the relationship between electrophysical, mechanical properties, sensory activity and the structure of OIS formed.

Methods: thermomechanical analysis (TMA) was used to determine the deformation properties of OIS and their thermal stability, dynamic mechanical thermal analysis (DMTA) was used for the detection of mechanical relaxation processes; mechanical methods at compression and elongation were used for the determination of a creep, stress relaxation, strength, relative elongation and modulus of elasticity; thermogravimetric analysis (TGA) was used to study the thermal stability, thermal and thermal-oxidative decomposition; rheokinetic methods were used to study the kinetics of structure formation; two-electrodes method at DC was used for determining the conductivity σ_{DC}; impedance spectroscopy (IS) was used to determine the conductivity σ_{AC}; broadband dielectric relaxation spectroscopy (DRS) was used to study the dielectric relaxation processes; the absorption methods were used for determining the sorption activity, sensory methods were used to study the sensitivity levels, an optical microscopy was used to study the microstructure of OIS; computer modeling was used for creating spatial structural models and models of conductivity of OIS.

Scientific novelty of the results:

- the mechanism of the structure formation of hybrid organic-inorganic systems based on urethane oligomers and silicates and the impact of organic component reactivity on the structure and properties of the formed hybrid systems were determined;
- for the first time the abnormal extreme nature of the kinetic parameters during structure formation of the investigated hybrid organic-inorganic systems was revealed;
- for the first time it was determined that the conductivity of hybrid systems involves three mechanisms of charge transport: proton conductivity, ion conductivity and conductivity of the matrix;
- for the first time high sensory activity and selectivity of hybrid systems to vapors of different types of solvents were revealed;
- the spatial structural model and the model of conductivity of this type of hybrid systems were developed.

The practical significance of the results is the determination of the impact of organic component reactivity on the structure of hybrid organic-inorganic polymer systems with the possibility of obtaining of the materials with predictable special properties. The results can be used as scientific basis for understanding the interconnection of structure, properties and ways of their directional regulation of hybrid organic-inorganic polymer systems. Whereas, the extremely high sensitivity to different types of solvents, which combined with the high selectivity, was revealed for the synthesized systems, the possibility of their practical use as sensor materials exists.

Applicant's personal contribution in the presented thesis is the search and analysis of literary data, creating and upgrading the equipment, carrying out theoretical and experimental research, analysis, interpretation and generalization of the results, formulating the conclusions, development of the theoretical models. Problem definition and determination of the research objectives, a part of theoretical and experimental studies were performed in conjunction with Head of department of polymer composites of Institute of Macromolecular Chemistry of NAS of Ukraine, Academician, Professor Lebedev E.V. and the research supervisor, Doctor. Sci. Mamunya Ye.P. in collaboration with Doctor Ishchenko S.S., Doctor Davydenko V.V., Doctor Shandruk M.I. in the department of polymer composites of Institute of Macromolecular Chemistry of National Academy of Science of Ukraine (Kyiv, Ukraine). Planning and execution of theoretical and experimental studies were also performed in conjunction with scientific supervisor, head of research CNRS, Doctor Boiteux G., involving Director of Laboratory of polymer materials and biomaterials of University Claude Bernard Lyon 1, CNRS, France, Doctor Seytre G., Professor Cassagnau Ph., Doctor Rybak A. in Laboratory of polymer materials and biomaterials of University Claude Bernard Lyon 1, CNRS, France (Lyon, France). Applicant took a part in preparation of publications and presentation the results on international conferences and symposia.

Approbation of the results. The main directions and results of the thesis were submitted on 26th International Conference “Composite materials in the industry" (Yalta, Ukraine, 2006), International Conference “Materials and Coatings under extreme conditions MEE-2006" (Yalta, Ukraine, 2006), 4th International Conference "IDS/DRP BDS – 2006” (Poznan, Poland, 2006), International Conference “Clusters and nanostructured materials CNM'2006" (Uzhgorod, Ukraine, 2006), 3rd International Conference of Young Scientists “Modern problems of polymer science” (St. Petersburg,

Russia, 2007), 5th Ukrainian Conference "VMS-2007" (Dnepropetrovsk, Ukraine, 2007), 9th European Symposium on Polymer Blends (Palermo, Italy, 2007), 3rd International Symposium "Reactive Polymers in Inhomogeneous Systems, in Melts, and at Interfaces" (Dresden, Germany, 2007), 4th International Symposium on Nanostructured and Functional Polymer-Based Materials and Nanocomposites (Rome, Italy, 2008), International Symposium "E-MRS International Symposium, European Materials Research Society Spring Meeting" (Strasbourg, France, 2008), 5th International Conference "IDS/DRP BDS-2008" (Lyon, France, 2008), 6th Ukrainian conference "VMS-2008" (Kyiv, Ukraine, 2008), 5th International conference on nanostructured polymers and nanocomposites (Paris, France, 2009), 17th World forum on advanced materials "PolyChar17" (Rouen, France, 2009).

Publications. 20 scientific applications, including 5 articles in scientific journals, 1 patent, 14 abstracts and materials of the conferences were published by results of the research.

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Modern conception of synthesis, structure and properties of hybrid organic-inorganic polymer systems (LITERATURE REVIEW)

Chapter 1

Modern conception of synthesis, structure and properties of hybrid organic-inorganic polymer systems

1.1. Classification and synthesis of hybrid organic-inorganic polymeric materials

1.1.1. Classification of hybrid organic-inorganic polymer systems.

Nowadays the term "hybrid materials" is used for many different systems, thus covering a wide range of polymeric materials such as polymer composites, materials with or without interaction between the organic and inorganic components. The broadest definition of hybrid material has the form [1]:

hybrid material is a material, which structure includes two parts that are mixed at the molecular level.

Basing on this definition of hybrid material it is possible to offer a generalized definition of hybrid organic-inorganic system:

hybrid organic-inorganic system (OIS) is a system, which structure includes both organic and inorganic units that interact with each other (Table 1).

Table 1. Possible compositions and structures of hybrid materials

Matrix	crystalline ↔ amorphous organic ↔ inorganic
Building blocks	molecules ↔ macromolecules ↔ particles ↔ fibers
Interactions between components	strong ↔ weak

The hybrid organic-inorganic systems can be conditionally divided into two classes using interaction between organic and inorganic blocks as the classification [1] (Fig. 1).

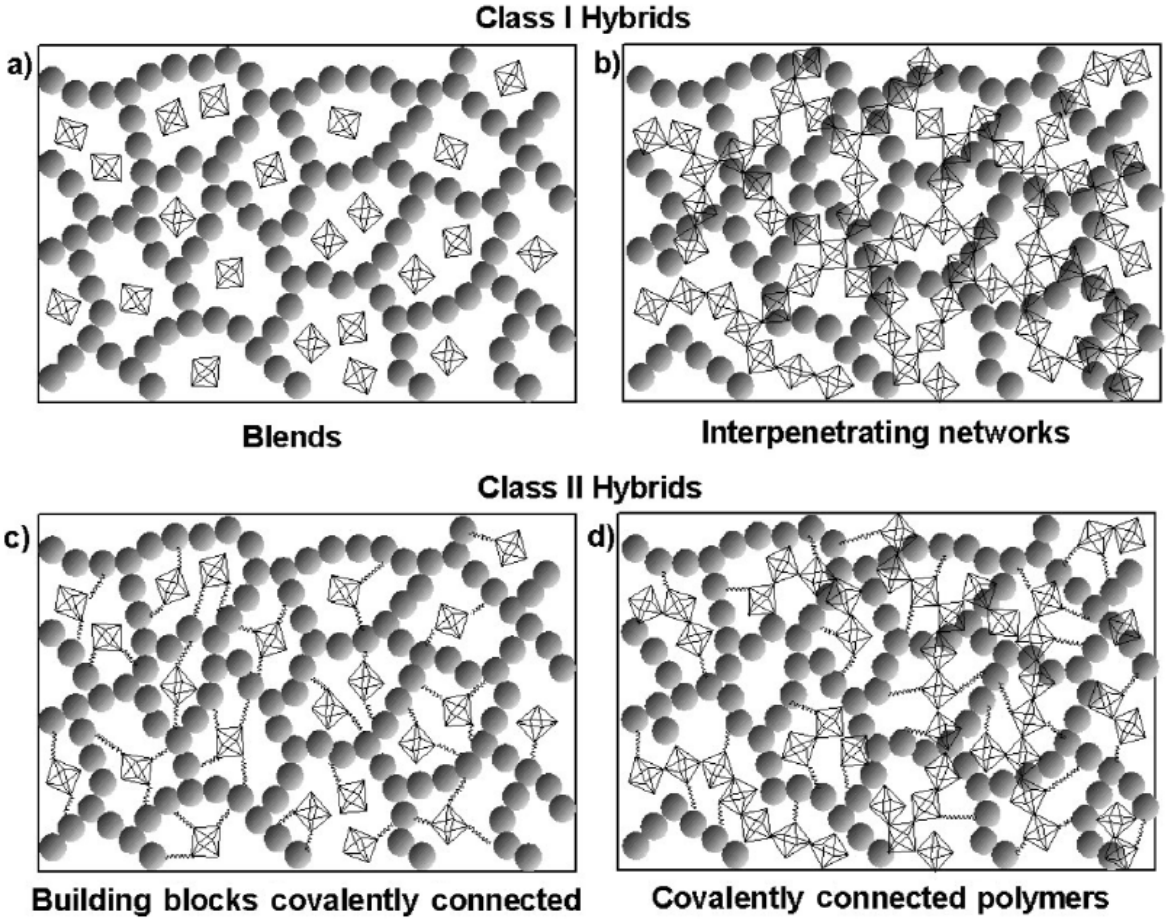

Fig. 1. The different types of hybrid materials.

Class 1 of hybrid systems are characterized by weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions (Fig. 2). Table 2 shows the classification of chemical bonds, depending on the energy of interactions. When the strong chemical interaction between organic and inorganic blocks is absent, the blend is formed (Fig. 1a). An example of such hybrid systems can be cross-linked polymer matrix with the inclusions of inorganic clusters or particles that have only physical interactions with the polymer [2, 3]. In the case, when the organic and inorganic networks interpenetrate each other, without forming strong chemical interactions, the structure of such system has the form of interpenetrating networks (Fig. 1b). Both cases belong to the class 1 of hybrid systems. For class 2 of hybrid systems the strong chemical interaction between organic and inorganic blocks is inherent, when inorganic structural units, clusters or particles covalently bonded to an organic matrix (Fig. 1c) or inorganic and organic polymers covalently connected with each other (Fig.1d). Using the example of

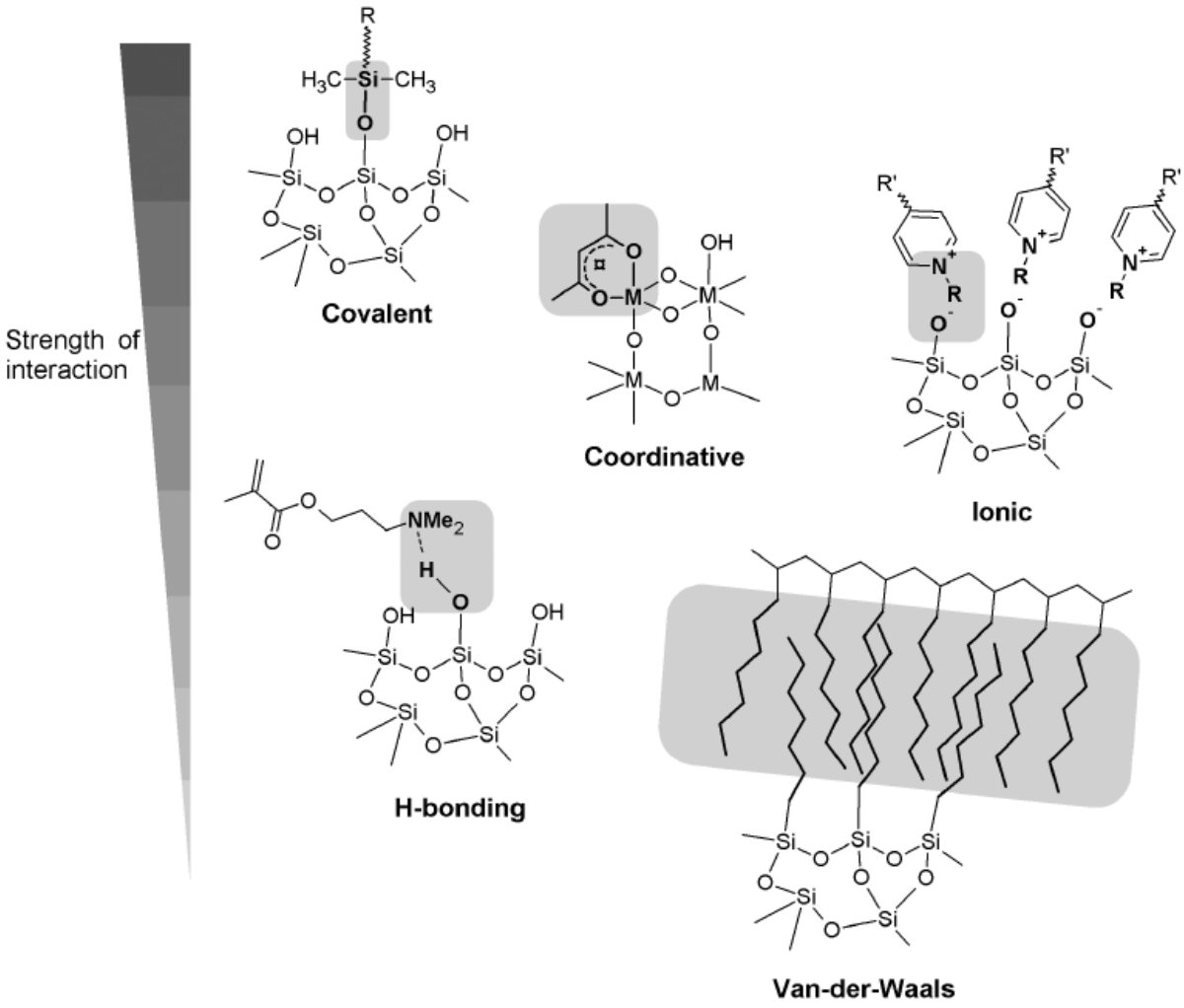

Fig. 2. Selected interactions typically applied in hybrid materials and their relative strength.

Table 2. Chemical interactions and their respective strength

Type of interaction	Strength kJ/mol	Range	Character
van der Waals	< 50	Short	nonselective, nondirectional
H-bonding	5-65	Short	selective, directional
Coordination bonding	50-200	Short	directional
Ionic	50-250	Long	nonselective
Covalent	350	Short	predominantly irreversible

phenyltrialkoxysilanes the impact of the structural organization of inorganic component on the overall structure of the hybrid system can be shown (Fig. 3).

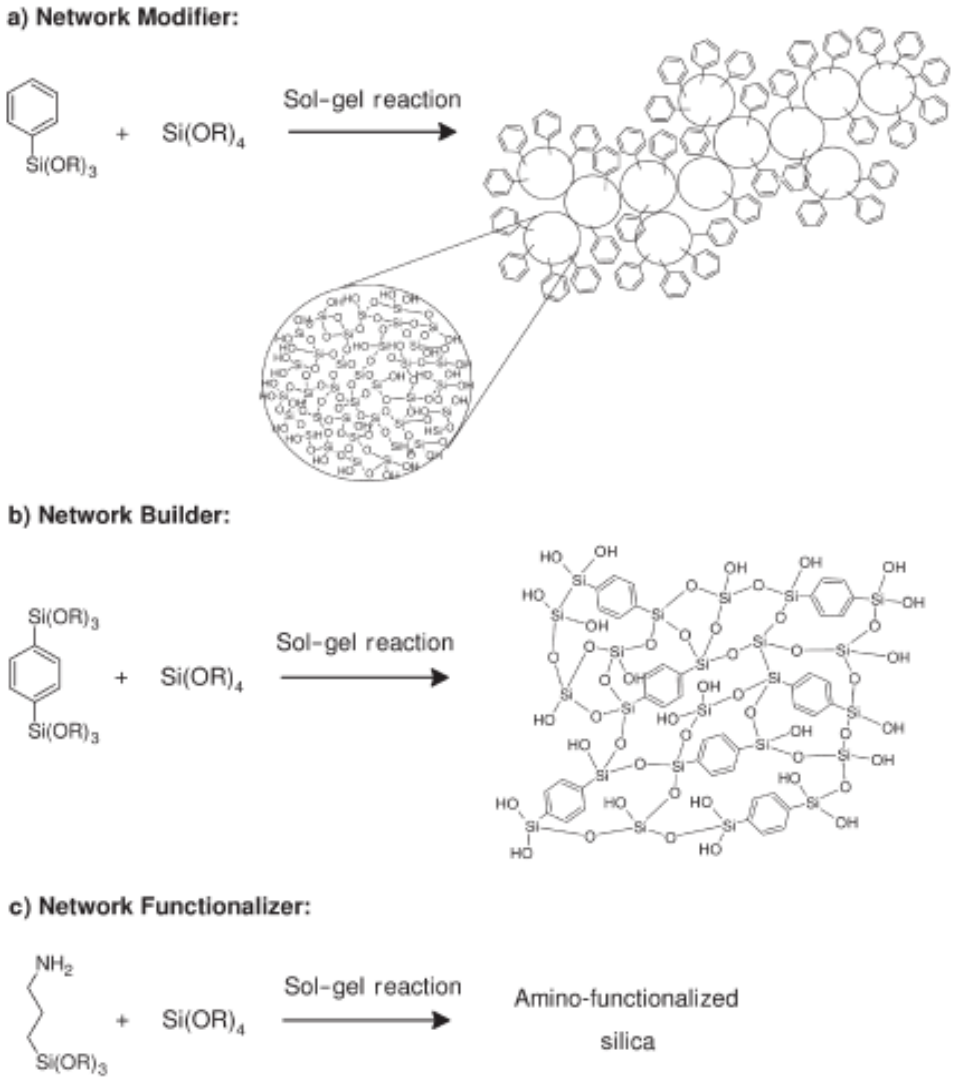

Fig. 3. Role of organically functionalized trialkoxysilanes in the silicon-based sol-gel process

When the silicon network is modified during sol-gel process through reactions of trialkoxysilanes groups without the presence of additional functional groups, the organically functionalized trialkoxysilanes play the role of network modifier (Fig. 3a). If the reactive functional groups are separated, then such system is called network functionalizer (Fig. 3c). Otherwise, two or three reactive groups modify the organic segment that leads to the formation of structure in which the inorganic groups are part of the hybrid network (Fig. 3b).

1.1.2. Synthesis of hybrid organic-inorganic polymer systems.

Analysis of literature data [1] gives the opportunity to highlight three main ways of synthesis of organic-inorganic hybrid systems (Fig.4): using sol-gel process, using pre-formed inorganic structural blocks and polymerization with simultaneous formation of both components.

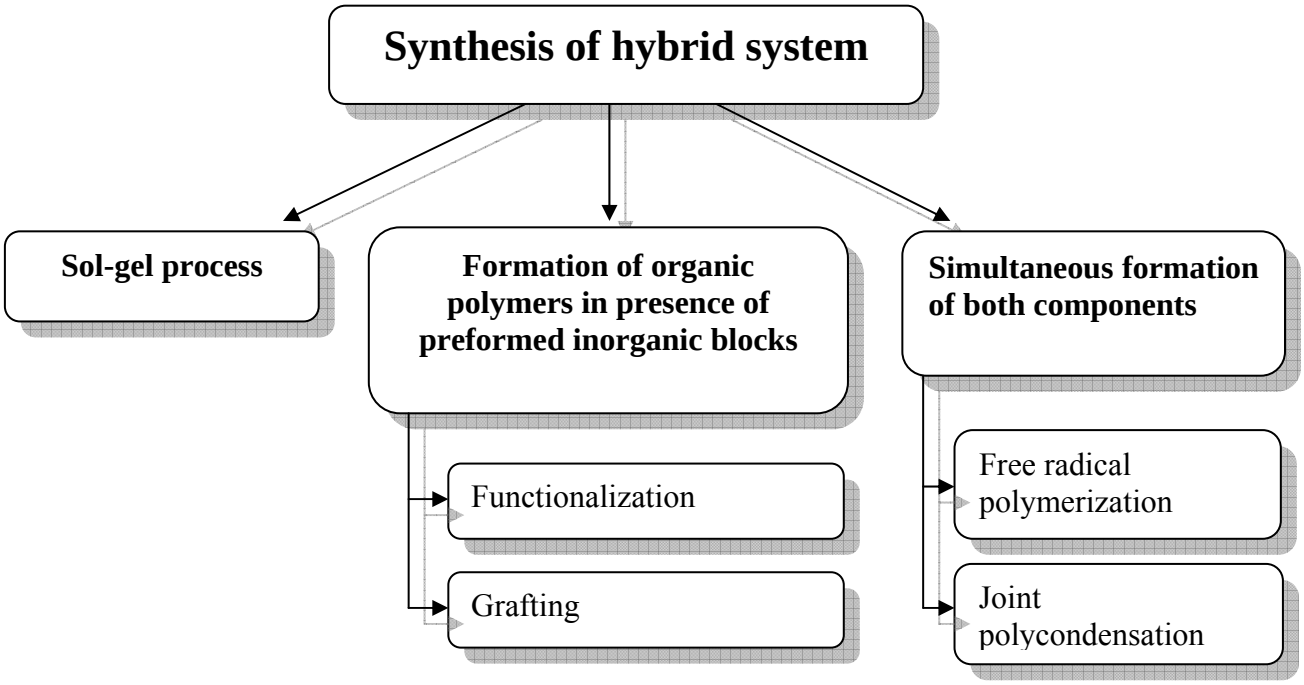

Fig. 4. Ways and methods of synthesis of hybrid systems.

Sol-gel process [4-19] (Fig.5) is chemically related to the polycondensation reactions of organic molecules in which small molecules form a polymeric structure due to the loss of substituents. At the first stage, during gelation, when the sol (colloidal dispersion of solid nanoparticles in liquid) passes into the wet gel (gel, which contains continuous solid and liquid phases), nanoparticles are grouped and form inorganic skeleton. Thereafter, depending on drying conditions, two different structures of dry gel - aerogel or kserogel are formed. Dry gel can be functionalized to join the reactive groups on the surface of the gel. The hybrid system is formed in the reactions of organic gel and the corresponding component. Usually sol-gel process leads to the formation of three-dimensional cross-linked network [1]. Using small molecules as precursor for the formation of cross-linked structure implies several advantages, such as high control of the

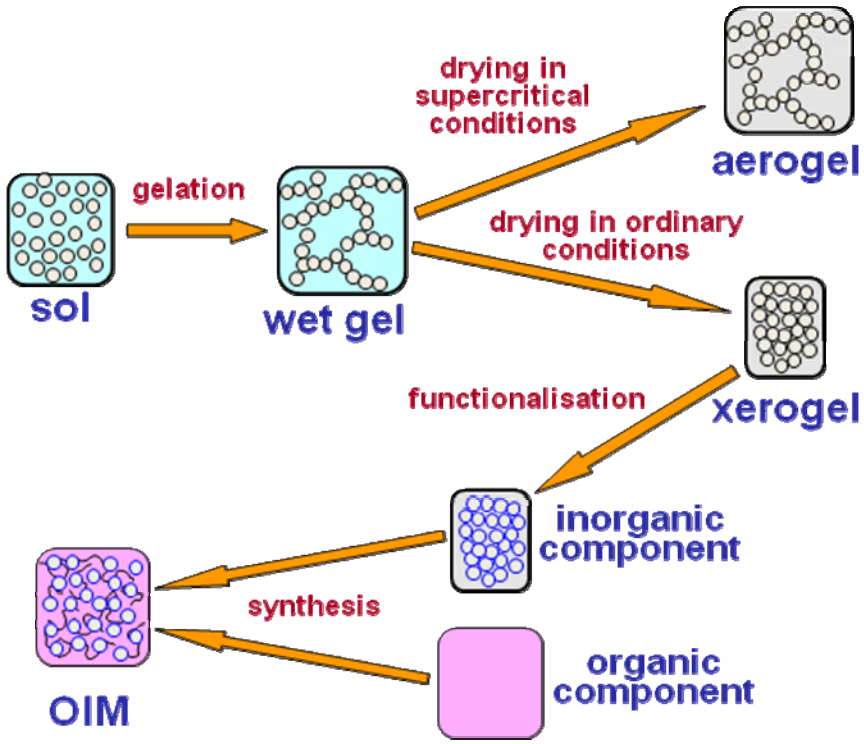

Fig. 5. Schematic diagram of one of the routes of sol-gel technology for obtaining OIS.

purity and composition of final products, the use of a solvent based chemistry which offers many advantages for the processing of the material formed.

The silicon based sol-gel process is the most studied, therefore the fundamental principles of reactions are usually described using the process as a model system [1] (Fig. 6). $R_{4-n}SiX_n$ compounds (n = 1-4, X = OR') used as molecular precursors, in which the Si-X bonds is labile to hydrolysis reactions and forms unstable silanols (Si-OH) that condensate leading to Si-O-Si bonds. In the first steps of this reaction oligomers and polymers as well as the cycles are formed subsequently resulting in colloids that determine the sol. Solid particles in the sol afterwards undergo cross-linking reactions and form the gel.

The second way of synthesis of hybrid systems is conditioned on the presence of pre-formed inorganic structural blocks [1]. This way consists two methods of the preliminary surface modification of inorganic structural blocks [20-24]: *functionalization* [25-31] (increasing the number of functional groups on the surface of inorganic block) and

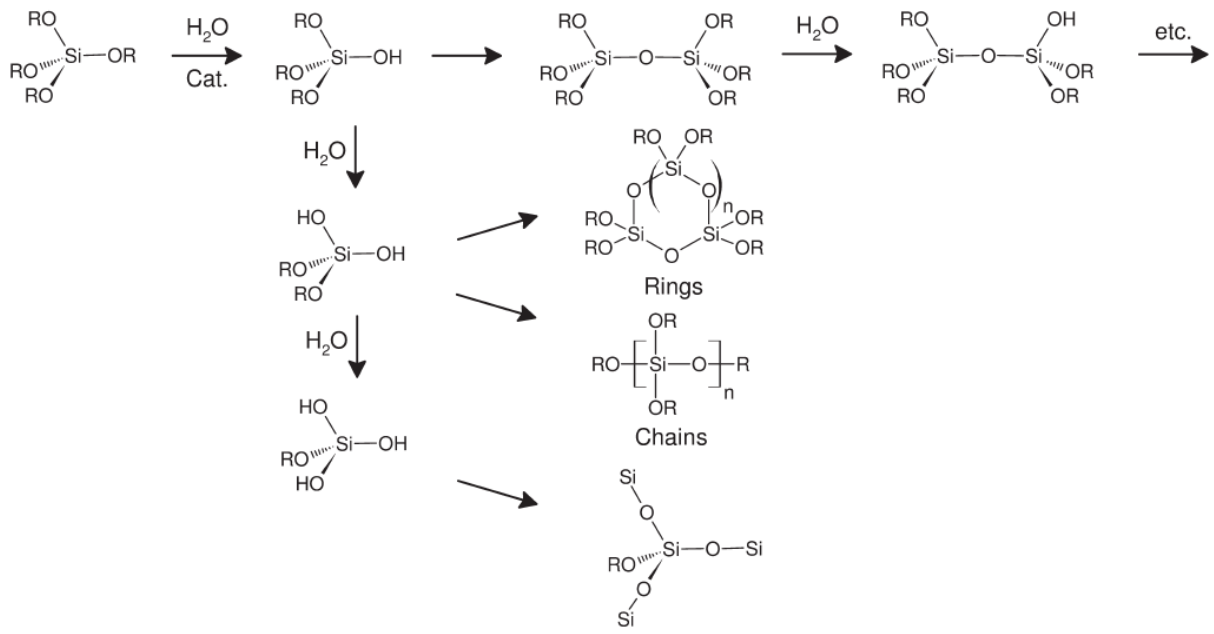

Fig. 6. Fundamental reaction steps in the sol-gel process based on tetrialkoxysilanes.

grafting [22, 32-37] (grafting end functionalized polymer to the surface of inorganic block). Surface *functionalization* can be done *in situ*, i.e. during formation, and *post-synthetic,* when the inorganic blocks have been already formed, while the *grafting* applies to post-synthetic process only. Using the example of polyhedral silsesquioxane (POSS) $R_8Si_8O_{12}$ [38-40], which received widespread use due to the possibility of modifications of Si-O clusters by different types of functional groups, the formation of inorganic structural blocks is shown (Fig. 7). Depending on the number of reactive functional groups the hybrid systems with different structures can be obtained. Fig. 8 represents the scheme of grafting of polyacrylamide to the surface of inorganic block by atom transfer radical polymerization.

Depending on the placement of organic functional groups on the surface of inorganic structural block the hybrid organic-inorganic systems with different types of structures are formed during the polymerization [34] (Fig. 9). The presence of one organic functional group on the surface of inorganic structural block leads to the formation of hybrid systems with linear structure. Formation of the cross-linked hybrid system is a consequence of the use of inorganic structural block with multiple organic functional groups. When the inorganic building block plays the role of initiator for the polymerization reactions, hybrid system will be in the form of organic phase grafted to inorganic core.

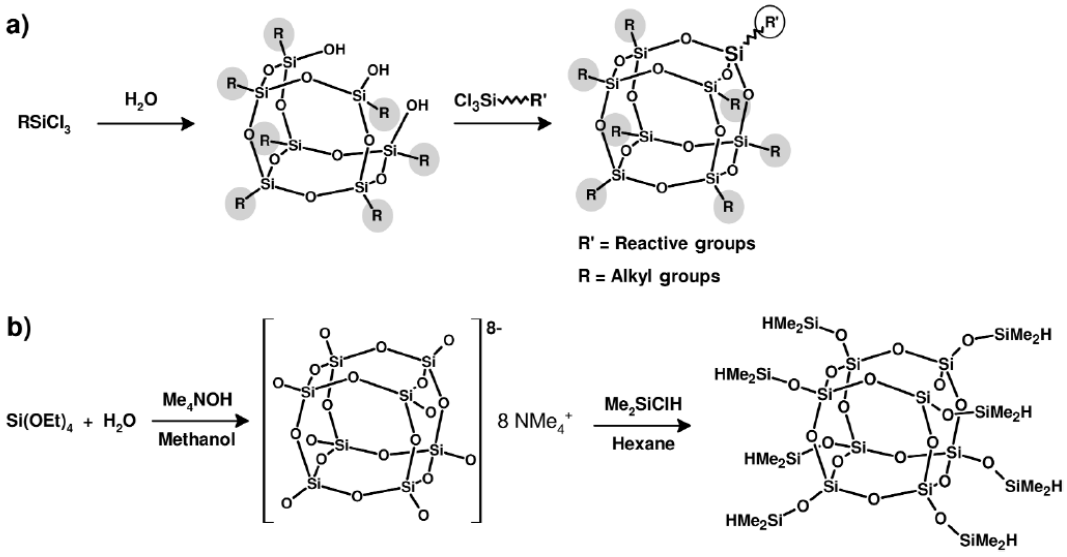

Fig. 7. Formation (a) and modification (b) of inorganic structural block.

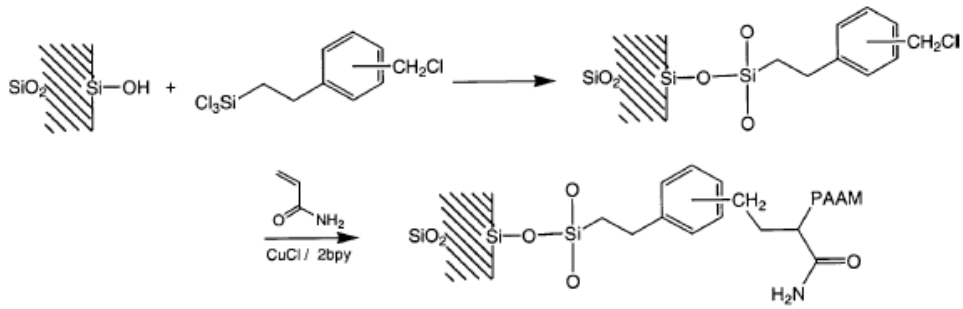

Fig. 8. Grafting of polyacrylamide to the surface of inorganic block.

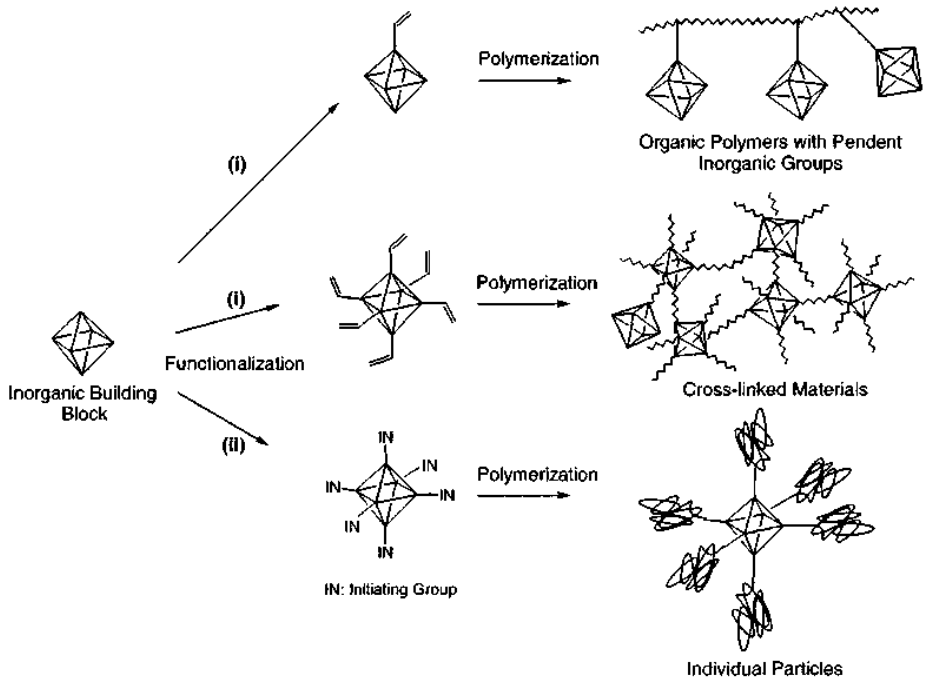

Fig. 9. Possible structures of hybrid systems synthesized using pre-formed inorganic structural blocks.

If the surface of inorganic block is not modified, it may contain nonreactive organic groups (e.g. alkyl chains) attached to its surface [1]. In this case, inorganic material can be dissolved in a monomer which is subsequently polymerized. The resulting product after organic polymerization is a blend, the inorganic component has only very weak or no interactions with organic polymer, other words class 1 of hybrid systems is formed. The strongest interactions occur if class 2 of hybrid systems is formed, provided the formation of covalent bonds.

The third major way of synthesis of hybrid systems is a process with the simultaneous formation of both components [1], i.e. organic and inorganic polymers that is revealed in obtaining the most homogeneous types of interpenetrating networks. Typically, for example, for sol-gel process precursors are mixed with organic monomers for organic polymerization and both processes take place simultaneously with or without solvent. Thus, three processes are competing with each other: hydrolysis and condensation forming the inorganic phase, polymerization of organic phase and thermodynamics of the phase separation between the two phases. This way includes two methods (see Fig.4): free radical polymerization [24, 41] (including atom transfer radical polymerization [42, 43], which was reviewed earlier) and the joint polycondensation. The mechanism of free radical polymerization is very intense and leads to very homogeneous materials (Fig.10) [1], but only selected monomers can be used for this process.

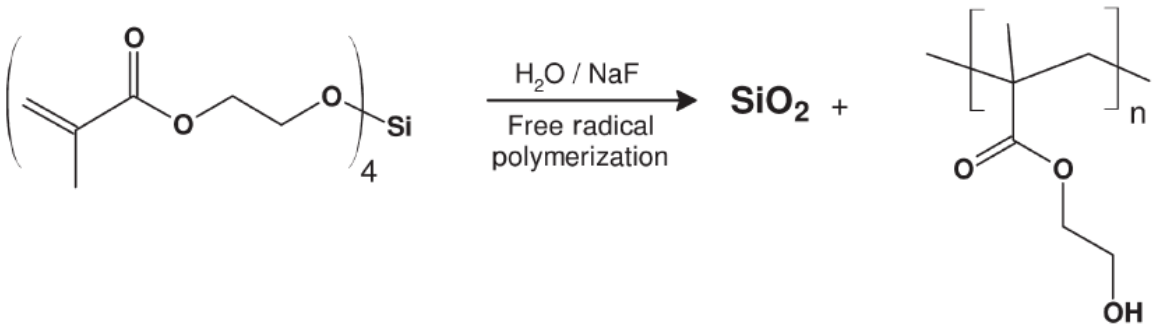

Fig. 10. Silicon sol-gel precursors with polymerizable alkoxides for free radical polymerization.

Formation of hybrid organic-inorganic systems by joint polycondensation of organic and inorganic components can be attributed to processes with simultaneous formation of both components. Joint polycondensation was developed in the Institute of Macromolecular Chemistry of NAS of Ukraine. The distinguishing feature of this method is the simultaneous polymerization of organic and inorganic components in their reactive

mixture due to the presence of reactive groups in both organic and inorganic components, without their prior modification [44-47].

Besides the major reviewed methods of formation and modification of hybrid systems less extended methods exist. Some of them are described in [48-65].

1.2. Thermomechanical properties of organic-inorganic polymer systems

The term "*thermomechanical*" is significant and contains all the mechanical properties of materials in a wide range of temperatures, pressures, frequencies etc., and includes static thermomechanical, dynamic thermomechanical, mechanical etc. investigations which, in turn, are common methods of studying the structure and behavior of materials under various conditions. Information of material characteristics such as hardness or elasticity [66, 67], the ability to elongation and compression [66-68], the relaxation and creep [69, 70], dynamic and complex viscosity [69], presence of structural modifications and transitions depending on temperature and composition [67, 68], strain energy [71] and, in some cases, existence of specific structural formations in the material, acceleration and ability of mechanical degradation [72,73] can be obtained using these methods. In [74-86] authors considered the existing theoretical models of mechanical deformation, creep and relaxation of elastic, viscoelastic materials and polymers, and methods of their investigation. Some changes to the well-known models, equations and methods of investigation were suggested. New models were presented and their theoretical justifications were provided.

In the paper [66] the properties of organic-inorganic polymer composites obtained by dispersion and doping methods of filler in polymer matrix, which was polyethyleneoxide PEO with the dispersed lithium salts $LiClO_4$, were studied. The silicate SiO_2, mesoporous silicate SBA-15 and mesoporous silicate P123@SBA-15 were used as the filler. Mechanical investigations of the synthesized OIS were performed at elongation and showed that the increasing the content of filler SBA-15 leads to reduction of relative elongation of the material with simultaneous increasing its strength. Similar work is [87]. However, unlike [66], the hybrid systems have been synthesized by sol-gel method and sulfonated fluorinated polymer SDF-F based on decafluorobiphenyl and 4,4

(hexafluoroisopropylidene)dephenol was used as the matrix. The results of mechanical investigations showed the strength decreasing with the increasing the content of inorganic component SiO_2 in the volume of organic SDF-F matrix. At the same time, SDF-F and SDF-F containing 4% SiO_2 showed improved strength characteristics comparing with known solid electrolyte Nafion. The investigation of mechanical properties of hybrid systems, which contain modified inorganic component, were carried out in [88-90]. In [88] the organic-inorganic system in the form of thin films, which were synthesized based on tetraethoxysilane TEOS, which was previously modified, were studied. New method of mechanical tests – nanoindentation was used by authors for determination the rigidity and Young modulus of the material obtained. This method was developed for studying the mechanical properties of thin films, because the use of classical methods of mechanical investigations was found impossible due to very small thickness of working area of the material (10-1000 nm). The main concepts of nanoindentation are the use of minimal loading and penetration of indentor (within nanometers) and high sensitivity of electronic mechanical analyzer. It was shown that the mechanical characteristics of samples tended to decrease, due to increasing the porosity of the materials obtained with the decreasing number of connections C-H and C-C and the increasing number of Si-O connections in the structure of thin films that was achieved by decreasing the temperature of annealing during formation of the material. Authors of [89] investigated bioactive organic-inorganic system synthesized by sol-gel method, based on methacryloxypropyltrimethoxysilane MPS and 2-hydroxyethylmethacrylate HEMA, which were modificated by simulated body fluid SBF (Kokubo solution). The investigation of mechanical properties of obtained systems showed the possibility of synthesis of materials with different levels of strength, which, in most cases, have higher values compared with similar biomaterials, depending on the composition of organic-inorganic systems and content of various types of SBF. Authors of [90] studied the organic-inorganic systems based on polyamide PA-6 that were obtained by the original one-step method. Cement-based precursor montmorillonite MMT and ε-caprolactam were used as inorganic component. Results showed that organic-inorganic systems with nanointerphases were synthesized by proposed method. Nanohybrids with high mechanical properties were obtained by further modification of the synthesized systems, and the necessary content of nanointerphases for such characteristics was not less than 15%.

The hybrid organic-inorganic materials, which were synthesized in reactive mixture of organic and inorganic oligomers, were studied in [91]. Urethane oligomers with different molecular masses were used as the organic components. Sodium silicate, which exists in the form of oligomer in aqueous solution, was taken as inorganic component. Parameters obtained from the mechanical investigations, which were carried out by dynamic mechanical thermal analysis, authors used for comparison with the parameters identified by other investigation methods. It was given the values of different glass transition temperatures of the compositions that were determined using dielectric and calorimetric investigations. It was shown that increasing the molecular weight of organic component and content of inorganic phase in OIS volume leads to significant reduction of the glass transition temperature values.

The main purpose of [92] was to study the properties of materials that may be promising as solid electrolytes for fuel cells. In this paper, hybrid organic-inorganic membranes were obtained from commercial product polyetheretherkitone PEEK that was previously modified and further mixed with Si-containing component. The research results of sulfonated polyetheretherketone SOSI-PEEK authors compared with the characteristics of known electrolyte Nafion. Mechanical studies showed that the synthesized material SOSI-PEEK has higher strength and much lower values of deformation at elongation compared with Nafion.

The hybrid systems based on epoxy resins and modified nano-SiO_2 precursor synthesized by sol-gel method and doped with carbon filler were studied in [93]. Mechanical investigations showed that with increasing the filler content and the change of nanoparticle dimensions strength of the systems grew in parallel with the increasing the matrix packaging value. Similar studies were carried out in [94], but unlike [93], the thermosensitive polyurethane was used as a polymer matrix here. Mechanical properties of the synthesized systems were studied at elongation. Authors showed that with increasing the content of SiO_2 nanoparticles in the bulk of compositions strength and their elongation at break grew rapidly due to connections Si-C and Si-O-C and acquired their maximums at 5% mass parts.

In [55] the industrial polypropylene PP, polybutylacrylate PBA and their mixtures were used as the polymer matrix. The nanoscale particles SiO_2 (aerosil) as well as in the previous papers and previously modified particles SiO_2 were inorganic component. Hybrid

organic-inorganic systems were obtained by mixing the polymeric and inorganic components. Previous modification enabled authors to obtain the systems with chemically bonded components. Mechanical studies showed that creep of the systems, which were filled with nanoscale particles SiO_2, decreased in comparison with pure polymer, while the systems with chemically bonded components showed even lower values of creep, i.e. the rigidity of the systems increased.

The broad studies of thermomechanical properties of different hybrid organic-inorganic systems have been carried in [95-103]. Authors used various methods of thermomechanical investigations. Among the most popular dynamic mechanical thermal analysis (DMTA) can be highlighted. In [95] hybrid organic-inorganic materials based on polyurethane, polymethylmetacrylate PMMA and tetraethoxysilane TEOS synthesized by sol-gel method were investigated. Mechanical studies were carried using DMTA, which allowed authors to explore the properties of the synthesized materials in broad temperature and frequency ranges. Studying the properties of systems depending on their composition passed in two ways. In the first case the influence of content of organic component, which consisted of two products (polyurethane and PMMA) and gradually changed, on the properties of the material was explored, while correlation between the organic and inorganic components remained constant. In the second case, authors investigated the influence of inorganic component on the properties of the synthesized systems, while the ratio between organic and inorganic components was sequentially varied. In the first part, it was shown that the increase the content of PMMA in organic component of hybrid systems leads to the rapid growing of the stiffness. The results of mechanical studies of the second part of the work allowed saying that the rigidity decreased with the increase of inorganic phase in the volume of such systems.

Authors of [96] studied organic-inorganic systems based on polyimide PI prepared from pyromellitic dianhydride PMDA and 4,4-oxydianiline ODA, organically modified montmorillonite OMMT and polydimethylsiloxane PDMS, which were synthesized *in situ* by sol-gel method. Mechanical and dynamic mechanical studies showed the improved mechanical properties of hybrid systems in comparison with the results of separately made components. Thus, hybrid systems have higher values of elasticity, strength and elongation at break. The reduction of glass transition temperatures with increasing the structural heterogeneity was found for hybrid systems.

In [97-99] the hybrid organic-inorganic polymer systems synthesized on polyhedral oligomeric silsesquioxane POSS were investigated by DMTA methods. In [97] authors studied the hybrid system based on epoxy resins and modified POSS. During the investigations the concentration dependences of mechanical parameters such as the mechanical loss tangent tan δ, elasticity modulus E′ etc. on temperature were constructed. Results showed that values of glass transition temperatures decreased with the injection of modified POSS into polymer matrix. Authors explain this phenomenon by the rise of free volume with increasing POSS content in the material. Paper [98] is similar to previous work. Just as in [97] authors investigated hybrid organic-inorganic systems, which included the epoxy resin and POSS. Mechanical properties of hybrid systems were studied by dynamic and static methods. As in the previous paper, authors constructed the concentration dependences of mechanical characteristics. It is interesting that unlike [97], glass transition temperatures of these systems increased with the injection of POSS. This inconsistency of the results may be explained by differences in the properties of modified and unmodified POSS, and their impact on the general properties of the systems. However, in [97] conclusions were made for the general case, detailed effects of POSS on the properties of hybrid system was not considered. Later, in the paper [98], authors examined the influence of POSS on the glass transition temperatures shift of hybrid systems and their mechanical properties. It was shown that the values of the glass transition temperatures increased with the rise of POSS concentrations, while the values of mechanical parameters increased only within the small concentrations of POSS (<10%) and rapidly decreased exceeding 10% of the mass part. In the paper [99] polyamine acid PAA was used as the polymer matrix of hybrid systems. Results of mechanical and thermomechanical studies showed that, as in the previous works, the rise of systems heterogeneity (increasing the content of POSS) led to deterioration of mechanical and thermomechanical properties of materials.

Another type of hybrid organic-inorganic polymer systems was studied by authors of [100, 101]. In these works porous polymers (polyHIPEs) were synthesized by polymerization of monomers and crosslinking co-monomers in the continuous phase of high internal phase emulsions (HIPE). Such hybrid systems are a new type of polymers, and, therefore, interesting to study. In the paper [100] monomer 2-ethylhexyl acrylate EHA and crosslinking co-monomer divinyl benzene DVB, tetraethylorthosilicate TEOS and sorbitan monooleate SMO were used as the components for synthesis of hybrid systems.

Mechanical investigations showed that the formation of hybrid polymer-inorganic interpenetrating networks leads to increasing the temperature and intensity of maximum of mechanical loss tangent tan δ. It is also shown that the elasticity modulus and plateau of highly elastic strain increased with the increasing of TEOS content in the compositions. Similar work is [101], in which authors studied polyHIPE systems that combined silsesquioxane SSQ and organic conductive polymeric (polypyrrole PPy, polyaniline PANI) networks. As a result, similar to the previous work, the interpenetrating organic and inorganic networks have been obtained. DMTA investigations showed that the mechanical properties of hybrid systems at high temperatures (> 250 ^{o}C) strongly depended on the content of SSQ, while at room temperature (≈ 30 ^{o}C) mechanical properties were independent on the content of mineral phase subject to the presence of organic rigid network. When such network was absent in the systems, mechanical parameters were dependent on the content of SSQ.

Among the variety of thermomechanical investigations nanoindentation method deserves special attention [102, 103], which has already been mentioned [72, 88]. Nanoindentation is new and very promising method, as it allows to study the behavior of materials at the lowest load and deformation and, in some cases, to detect and investigate nanostructural formations in its volume. In [72, 102] the hopping creep was studied using this method, which reflects the heterogeneity of the structure at meso-and nanolevels of amorphous polymer systems. Epoxy resin D-450 and PVC were used as the polymer matrix, and diabase particles were used as nanoscale inclusions. Using laser interferometer authors registered the speed of creep at submicron transformations during compression. It was found that periodic fluctuations of speed depending on time or deformation correspond to the discontinuous nature of deformation. Thus, it was experimentally shown that diabase particles resulted in appearance of jumps in creep with the same scale, while jumps of deformation at nanolevel related to the globule sizes. Authors showed that the study of jump deformations gives the opportunity not only to assess the formation of micro-and nanolevels in amorphous polymers, but to make conclusions about the connections between ordered structures.

In the paper [103] the investigations of properties of hybrid organic-inorganic coatings based on tetraethoxysilanes TEOS, glycidoxypropyltrimethoxysilanes GPTMS and diethylenetriamine DETA, which were synthesized by sol-gel method, were carried out. Mechanical properties of materials obtained were studied using nanoindentation

method. Results of experiments showed that the coatings, which were obtained with the ratio TEOS/GPTMS equal to 80/20, had considerable rigidity and fragility. Values of mechanical characteristics of these systems increased with increasing the curing temperature up to 350 ^{o}C. Data obtained from the investigations of coatings, which were synthesized based on GPTMS and DETA, showed less rigidity and flexibility than previous. The rise of DETA content in compositions resulted in increasing the number of connections in organic network and values of mechanical parameters. It was found that presence of many connections in organic network inhibited thermal degradation that, in all cases, started at 250 ^{o}C.

1.3. Electrical and dielectric properties of organic-inorganic polymer systems

Fundamental studies of electric and dielectric properties make it possible to expand the range of information about materials and to obtain the information about molecular mobility, relaxation processes and ways of charge transport in materials etc. Among the leading sources, which reveal the fundamental principles and basic aspects of dielectric and electrical behavior of polymeric materials, [104-111] can be distinguished. Authors of [112, 113] reviewed in detail the theories and models of dielectric relaxation, molecular mobility and conductivity. Using of models and theories for description the real results of studies of electric and dielectric properties of polymeric materials is given in [114, 115].

Recently the ion (proton) conductivity of polymer materials acquired great popularity. Such a significant interest to this field of polymer physics can be explained by the possibility of obtaining the solid electrolytes and fuel cells based on ion- and proton conducting polymer systems and the perspectives of their implementation in industry and energetics as alternative ecological sources of energy [58, 65]. In the cited works the commercial hybrid material Nafion and its modifications were considered. The popularity of this material may be explained by the high ionic conductivity, which is uncharacteristic for pure polymers in general, and ionselectivity and cation-exchange properties that allow its use as the solid electrolyte as well as the fuel cell. Not less interesting to study the hybrid polymer systems that contain silicates SiO_2, ions of lithium, sodium, aluminum, etc. So in [18, 19] the properties of high-conducting polymer membranes with proton

conductivity, which may be promising for use in electrochemical equipment, were studied. Organic-inorganic nanocomposite membranes based on silicate SiO / polyethyleneoxide PEO, which were synthesized by sol-gel method, are known to be generally related to the family of isotropic, elastic, amorphous polymers. Hybrid membranes doped with protons and various ions are characterized by high conductivity at elevated temperatures (> 100 ^{o}C). Conductive membranes are generally stable at high temperatures due to the presence of inorganic component SiO in their structure. The conductive membranes synthesized in these works showed high proton conductivity ($\sigma \approx 10^{-4}$ S/cm at 160 ^{o}C) that allows to attribute them to the family of solid polymer electrolytes with proton conductivity, which can be implemented into the manufacturing process and used in high-temperature electrochemical devices such as fuel cells, displays, chemical sensors and others.

Authors of [116] studied the dielectric properties of hybrid organic-inorganic systems based on polyimide PI and silicate SiO_2, which were obtained in sol-gel reactions and thermally stabled. Results showed that the permittivity of the synthesized hybrid materials is in the range from 3,4 to 6,0. With increasing the content of inorganic component the permittivity of the systems grew rapidly. Thus, the possibility to control the dielectric properties and thermostability of the materials by variation of SiO_2 content that is perspective for the use of such hybrid polymer systems in dielectric equipment has been shown. The results were well described using Maxwell-Garnett model [117].

Di Noto et al. in [118] studied the hybrid organic-inorganic films based on polymethylmethacrylate PMMA and polyvinylchloride PVC as the polymer matrix and SiO_2 as inorganic component. Electrical and dielectric properties of the synthesized films were studied using dielectric spectroscopy. It was shown that the permittivity ε′ of the obtained materials was less 3,5 and the dielectric loss tangent tan δ was less 0,05 in the frequency range 40 Hz-10 MHz and temperature range 0-130 ^{o}C. Dielectric spectroscopy gave the opportunity to build the dependences of molecular relaxation in composites $[(PMMA)_x(PVC)_y]/(SiO_2)_z$ on the temperature and compositions of the systems. In fact, the the permittivity ε′ of hybrid films with $20<z<35$ mass percents was less compared with pure inorganic component SiO_2 (ε′=3,9, tan $\delta<0,05$). These results enabled authors to speak about the perspectives of implementation this material in microelectronic equipment.

Authors of [66] investigated hybrid organic-inorganic polymer composites based on polyethyleneoxide PEO, mesoporous silicate and lithium ions as the filler. Number of

lithium ions that conduct were determined by impedance spectroscopy combined with stabilized current technique, which was proposed by Vincent and Bruce [119, 120]. Results showed the possibility of increasing the ionic conductivity by increasing the number of lithium ions that conduct and creation a new way of lithium ions transport. This made it possible to consider this hybrid material as a promising electrolytic material for lithium polymer batteries.

In [121] authors investigated hybrid organic-inorganic polymer electrolytes based on polyethylene oxide PEO, SiO_2 and lithium salts $LiClO_4$ synthesized by sol-gel method. Electrochemical studies were carried out using impedance spectroscopy. Results showed that the obtained membranes doped with lithium salts have the significant electrical conductivity ($\sigma \approx 10^{-6}$ S/cm at room temperature) and with the elasticity and thermal stability can potentially be applied in the production of high-temperature electrochemical devices (displays, chemical sensors, fuel cells etc.).

In [122] the electrical properties of hybrid polymer materials based on polyethyleneoxide PEO and lithium salts synthesized by sol-gel method were studied. These hybrid organic-inorganic systems showed the improved values of dielectric characteristics in comparison with similar nonhybrid materials. It was found the possibility to charge/discharge hybrid systems at lower temperatures and higher values of current, whereas higher temperature and lower values of current were required for analogs. On the basis of lithium salts the ion conducting organic-inorganic polymer systems were also synthesized in [123, 124]. In [123] the hybrid systems that contain tetraethoxysilane TEOS, (3-glydicyloxypropyl)trimethoxysilane GLYMO, lithium salts $LiClO_4$ and poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) bis(2-aminopropyl ether) D2000 were synthesized using sol-gel method. The changes of dielectric properties were studied. The hybrid materials with very high ionic conductivity even at room temperature ($\sigma \approx 10^{-2}$ S/cm) were obtained. Authors of [124] investigated hybrid solvent free organic-inorganic solid polymer electrolytes, which were synthesized by sol-gel method. The commercial product d-U(900) based on oxyethylene oligomers was used as polymer matrix, which was filled with lithium bis(trifluoromethanesulfonyl) imide LiTFSI. Electrical properties of electrolytes were determined by the level of ionic conductivity using voltage-current characteristics. It was shown that the obtained solid polymer electrolytes are completely amorphous and can be used in electronic devices due

to its high ionic conductivity at room temperature ($\sigma \approx 10^{-4}$-10^{-1} S/cm) and electrochemical stability.

Authors of [11] studied organic-inorganic polymer systems based on polyethylene glycol 200 PEG_{200}, tetramethylortosilicate TMOS and lithium salts $LiClO_4$ obtained by sol-gel method. The possibility of using the synthesized systems as high density electrolytes on the basis of lithium salts was investigated. Ionic conductivity of the obtained systems was determined by complex impedance spectroscopy. The results showed that with increasing PEG_{200} content ionic conductivity increased, while in the hybrids without lithium salts the ionic conductivity was absent. Materials with the conductivity $\sigma \approx 10^{-5}$ S/cm at room temperature were obtained.

In the paper [12] the organic-inorganic polymeric materials based on tetraethoxysilane TEOS, polyethylene glycol PPG with and without covalent organic-inorganic chemical bonds doped with lithium salts $LiClO_4$, with general name ORMOLYTES (organically modified electrolytes), were synthesized by sol-gel method. Results of electrical studies showed that the authors obtained ion conducting ORMOLYTES with high ionic conductivity ($\sigma \approx 10^{-6}$ S/cm), that, together with optical and mechanical properties, makes it possible to use these materials in electrochemical devices. The rise of ionic conductivity with increasing silicate content in the bulk of polymer matrix was also found.

Similar paper is [13], in which authors also studied the family of Li^+ ion conducting hybrid organic-inorganic polymer systems called ORMOLYTES, which included tetraethoxysilane TEOS and polyethylene glycol PEG, obtained by sol-gel method. Using method of complex impedance spectroscopy the ionic conductivity of materials obtained as a function of polymer chain length and concentration was defined. It was revealed that the ionic conductivity decreased with increasing the polymer chain length, but increased with increasing the concentration of organic component. The highest conductivity ($\sigma \approx 10^{-2}$ S/cm) at room temperature were found for the sample with PEG/TEOS = 40% mass parts.

In the paper [15] somewhat different family of hybrid organic-inorganic materials entitled ORMOCERS (organically modified ceramics as polymer electrolyte) based on organically modified polysiloxane monomer, which were obtained under the action of ultraviolet radiation in the presence of liquid electrolyte, were considered. Electrochemical properties of hybrid organic-inorganic polymer electrolytes were investigated by

impedance spectroscopy and cyclic voltage-current measurements. It was found that ionic conductivity strongly increased with increasing the amount of liquid electrolyte. So at 80% mass parts of liquid electrolyte conductivity equaled to $3{,}3 \cdot 10^{-3}$ S/cm at 21 ^{o}C and $8 \cdot 10^{-4}$ S/cm at -23 ^{o}C. Hybrid organic-inorganic polymer electrolytes also showed the extraordinary electrochemical and surface stability. Surface stability of the materials increased with time and achieved the best performance after 2 days. Stability of surface to oxidation was higher in contrast to lithium and steel electrodes.

Polyurethanes can also be used as polymer matrix for hybrid organic-inorganic polymer systems with ionic conductivity. Actually, systems based on polyurethanes are very interesting to study because they can be used as a model for investigation the formation of networks and processes of charge transport, mobility of chains and groups etc. For example, in [125] authors studied dielectric and electrical behavior of films with ionic conductivity based on polyurethanes by dielectric relaxation spectroscopy and conductivity on DC. It was shown that films with ionic conductivity were characterized by the presence of microphase separation on elastic and rigid microareas. To explain the results two mechanisms of conductivity were considered. It was suggested that the short relaxation times related to the elastic microareas and longer relaxation processes referred to hard microareas. It was shown that the fast relaxation mechanism of conductivity of elastic microareas accelerated the mechanism of conductivity relaxation of hard microareas.

To explain the properties of polyurethanes authors of [126] studied the evolution of the α-relaxation process during their polymerization by dielectric spectroscopy methods. It was determined that the form and temperature dependences of relaxation times were similar for pure triols, and their evolution during polymerization of polyurethane systems depended on the molecular weight of triols. This fact was explained by the transformation of active dipoles as the result of reactions and appearance of new dynamic connections between new active dipoles.

In the paper [91] authors investigated the relationships between microstructure, dielectric properties and molecular mobility of hybrid organic-inorganic polymer composites, which were obtained in the reactive mixture of polyurethane and sodium silicate. It was shown that the molecular mobility was higher in the composites compared with pure polyurethane matrix and electrical conductivity increased with increasing the content of inorganic phase or molecular weight of polyurethane.

Due to the different methods of formation of hybrid organic-inorganic polymer systems that were previously considered, it is possible to obtain hybrid materials with different organic and inorganic components, which have different structures and, therefore, properties [127-134]. In the paper [135] new hybrid solid polymer electrolytes, which included polyethylene oxide PEO, microphases of lithium salts LiTf and organically modified aluminosilicate OM-AlSi were studied. Impedance spectroscopy was used to study the conductivity and permittivity of obtained films. Results of experiments showed that the modification of aluminosilicates significantly affected on the conductivity of hybrid systems. Isolation of inorganic phase by reducing the dimensions of OM-AlSi domains increased interfacial area between OM-AlSi and PEO+LiTf. The presence of CN groups on the surface of OM-AlSi/PEO + LiTf increased the permittivity of interfacial layer and conductivity. At the same time temperature dependences of conductivity showed no change in the mechanism of conductivity of synthesized modified solid polymer electrolytes.

Obviously, due to wide range of characteristics and suitability of synthesis of hybrid organic-inorganic polymer materials with desired properties and prospects of their use in industry, new fundamental works, which examined the structure and conductivity mechanisms, are carried out, new models of ion and proton conductivity, and their theoretical basis are proposed, new ways and means of their introduction in industry are searched [61, 136,137]. Nowadays, some developed organic-inorganic hybrid systems are already patented and used in industry, despite the novelty of this field of polymer science [138-140].

1.4. Sorption and sensory properties of hybrid organic-inorganic polymer systems

Unlike the thermomechanical, thermal, electrical and dielectric studies, which are primarily used to study the structure and ways of charge transport in materials, investigations of sorption and sensory properties mainly cause a practical interest. Among the main areas of practical application of hybrid materials [141] with the specific sensory and sorption properties can be defined as follows:

- solid polymeric electrolytes for use in power sources [58, 60], which showed the effectiveness in comparison with salt and alkaline analogs;

- fuel cells, which are ecological alternative energy sources [142, 143];

- chemical and gas sensors [144-146];

- medications. This area can be conventionally divided into two trends: 1) the introduction of hybrid polymer materials for direct use in medical purposes [17, 137, 146] (the struggle with some viruses, the insertion in living tissues as implants, artificial bones, cartilages etc.); 2) the use of hybrid systems for transporting the drugs into the body («drug delivery»);

- construction and industry. In these spheres of human life the hybrid polymeric materials can be used as coatings, adhesives and others due to the presence of properties required for various needs that can be purposefully regulate. Among the most important heat resistance, fire resistance, chemical and radiation resistance, high adhesion to many materials etc. are emitted [147-149].

The major tenors of researchs of properties of hybrid polymer systems are:

- sorption properties (sorption of water and various types of solvents [63, 87, 88, 92, 150-152], swelling [153, 154]) and their influence on the conductivity (proton and ion) [57, 62, 142, 143,155, 156]);

- sensitivity to different gases and vapors of various substances [101, 157, 158];

- permeability of hybrid polymer materials [159 - 162];

In the paper [163] authors studied hybrid organic-inorganic polymer systems based on urethane oligomers and aqueous solution of sodium silicate, synthesized in the reactive mixture of organic and inorganic components. The aim of this work was to study sorption and electrical properties of the synthesized hybrid materials. It was shown that hybrid systems are characterized by high sorption capacity (up to 2000%) due to the presence of inorganic phase in polymer matrix. Cyclic sorption/desorption experiments showed good reproducibility and changing of the conductivity up to several orders of magnitude because of ionic conductivity due to the presence of inorganic phase and the adsorbed water. Also, authors showed that sorption and electrical properties depended on molecular weight of

organic component. Conductivity of hybrid systems increased with increasing the molecular weight, while the values of sorption characteristics contrary decreased.

In [164] scientists investigated hybrid polymer coatings based on acrylate/TiO_2 synthesized by sol-gel method. Sorption properties of the obtained systems were studied by methods of thermogravimetry and impedance spectroscopy. For description the obtained results authors used Fickian and Berens-Hopfenberg models [165], and Brasher-Kingsbury equation [166]. Comparison of the Fickian and Berens-Hopfenberg models gave to authors the opportunity to conclude that linear capacity increased at longer times of immersion that was explained by the slow relaxation of polymer chains during the process of water sorption. The change of water condition during immersion (increase of water clusters) was noted by authors as the another important factor that influenced on the long-term immersion.

In the paper [167] the hybrid organic-inorganic composite membranes based on two different polymer matrices: post-sulfonated poly(ether ether ketone) (SPEEK) and pre-sulfonated poly(aryl ether ketone) (SPAEK-6F) were studied. Nanoscale particles of boron phosphate (BPO_4) were used as an inorganic filler. Both systems were synthesized by sol-gel method. It was shown that the hybrid membranes based on SPEEK/BPO_4 had higher proton conductivity in comparison with the systems based on SPAEK-6F/BPO_4 at the same level of water sorption. This was explained by different particles sizes of inorganic phase BPO_4, which had a few micrometers in diameter in SPEEK compositions, while for SPAEK-6F size did not exceed a few hundred nanometers. Results showed very high proton conductivity at the level of known solid polymer electrolytes such as Nafion.

Similar work is [168], in which SPEEK and SPEK were used as the polymer matrix, but the inorganic components were SiO_2, TiO_2 and ZrO_2. It was shown that extraordinary reduction of permeability of methanol and water was achieved due to the insertion of inorganic component into the polymer matrix. The best balance between high conductivity and low permeability of methanol and water was obtained due to the decreasing the content of ZrO_2 and zirconium phosphate.

In [169] hybrid systems were synthesized based on poly(ether ether ketone) (SPEEK) sulfonated up to 90% and mixed with $SiCl_4$. The investigations of the structure using nuclear magnetic resonance and infrared spectroscopy methods showed the presence of covalent bonds between organic and inorganic components. Authors noted that the

formation of such hybrid materials made it possible to obtain membranes with high thermostability, unusual sorption properties and high electrical characteristics.

In the paper [170] the hybrid organic-inorganic materials based on SPEEK and organically modified montmorillonite (OMMT) were synthesized. Results of experiments showed that the obtained membranes are characterized by low swelling at high temperatures due to the separation of OMMT, high conductivity ($\sigma \approx 10^{-2}$ S/cm) at high temperatures and very low methanol permeability. Authors emphasized that the proposed membrane easy to produce, they are economically efficient, unlike the popular commercial analogs and can be qualified as composite membranes for fuel cells as an alternative to Nafion membranes due to high proton conductivity and low methanol permeability.

In regard to Nafion, in [60] its properties and properties of materials with its modifications (Nafion doped with TiO_2) were directly studied. It was found that modified membranes had higher conductivity compared to Nafion in vapor of water and gave the best performance in fuel cells. Water sorption was the balance between the energy of sulfation of sulfonate groups and energy for the swelling of membranes. Sorption of modified membranes based on Nafion increased with temperature rise, the membrane obtained sorbed water faster and more in comparison with extruded Nafion. Water sorption in Nafion membranes was revealed in increasing the swelling pressure. Thus, the swelling pressure of samples of Nafion 115 at 100% humidity and 80 ^{o}C equaled to 0,55 MPa, while it was almost insensitive to temperature changes.

In [171] the hybrid organic-inorganic nanocomposites based on 2-hydroxyethyl methacrylate (HEMA), poly(ethylene glycol) methylethermethacrylate (PEGMA) and methacrylic acid (MAA) synthesized by free radical polymerization with the insertion the fibrillar attapulgite in the polymer matrix were studied. It was found that the way of water transport in nanoscale hydrogel had abnormal non-Fickian character of diffusion. Nanoscale hydrogels showed much higher value of sustainable swelling compared with the correspondent cross-linked hydrogel. Content of inorganic phase also had an impact on the swelling. With increasing the content of inorganic component the swelling of the hybrid materials decreased.

Authors of [172] studied organic-inorganic composites with proton conductivity based on 3-glycidoxypropyltrimethoxy-silane as organic component and SiO_2, Al_2O_3 as inorganic components. Synthesized hybrid system showed high values of swelling in

methanol and water. It was found that materials obtained from the mixture of both inorganic components can be promising as membrane for use in fuel cells.

Authors of [173] studied the organic-inorganic membranes based on poly(styrene–NaSS–UAN) random copolymer (PSSU) consisting of a sulfonated monomer (NaSS) and a non-sulfonated monomer (styrene) and urethane acrylate non-ionomer (UAN). As a result of the synthesis membranes containing hydrophilic domains with 5-10 nanometers in diameter dispersed in nanodimensional hydrophobic polymer matrix were obtained. The hybrid membranes showed two-phase behavior of swelling during sorption of water and toluene due to such heterogeneous structure. It was found that with increasing the content of sulfonated monomer content the level of swelling, proton conductivity and permeability of materials increased.

In [174] the proton conducting organic-inorganic nanohybrids based on bridged polysilsesquioxanes doped with acidic moieties such as 12-phosphotungstic acid (PWA) synthesized by sol-gel method, were considered as the promising material, which has high proton conductivity ($\sigma \approx 10^{-2}$ S/cm) at high temperatures (up to 160 ^{o}C), for use as solid electrolytes. For the obtained membranes it was found that the conductive of material essentially depended on its humidity within temperature range from 120 to 160 ^{o}C, when conductivity decreased exponentially with the pressure of water vapors. Conductivity reached value $2 \cdot 10^{-3}$ S/cm even at 20% humidity and temperature 120 ^{o}C. Proton conductivity was stable above 100 ^{o}C with low dependence on humidity. Thus, organic-inorganic hybrids in this work showed the presence of constant channel of conductivity even in the structure of elastic macromolecules.

In the paper [175] scientists investigated the permeability of water vapors, oxygen in the organic-inorganic polymer coatings based on tetramethoxysilane, zirconium propoxide, aluminum-sec-butylate, 3-glycidoxyproyl-trimethoxysilane and 3-aminopropyltriethoxysilane, applied on biaxially oriented polypropylene (BOPP) films and coated with a thin layer of SiO_2- PET (polyethyleneterephthalate). The results showed the presence of a barrier to flavors (one layer) and water vapors and oxygen (two layers in combination with SiO_2) in synthesized hybrid organic-inorganic polymer films. Such materials can be used as coatings as well as highbarrier laminating agents in multilayered structures. It was shown that even after high mechanical and thermal stress and storage in humidity the composite film revealed excellent oxygen barrier properties.

Researchers in [176] studied the sensory properties of hybrid organic-inorganic materials based on polyaniline/Mn_3O_4 doped with organic-inorganic acids. It was found that the systems with imposed acids showed the rise of resistance with increasing the relative humidity, while the sensitivity depended on the type of doped anions. It was shown that the response of each composition was almost linear with respect to the level of humidity, but the compositions doped with organic acids were more sensitive compared to systems with inorganic dopants. However, polyaniline doped with the same acids in the same conditions showed the opposite behavior. The resistance decreased with increasing the relative humidity, but, in this case, the sensitivity was much lower. This anomalous behavior was explained by the presence of proton conductivity in polymer matrix with increasing the humidity. Thus, due to the linear dependence of resistance on humidity of composites doped with organic acids, such materials can be used as humidity sensors.

Apparently, the investigations of sorption and sensory properties, in terms of possible of using the hybrid organic-inorganic polymers as solid polymer electrolytes, which are characterized by improved characteristics in comparison with salt and alkaline analogs, as membranes for fuel cells, which attract a significant interest as alternative energy sources, as coatings for use in ordinary and extreme conditions (in space, under the effect of high radiation, temperature, active environments etc.), and as sensors.

In addition to studying the necessary properties of hybrid organic-inorganic systems, theories and methods of their applications are actively developed. For example, in [177] authors proposed to use the hybrid systems as gas barriers (coatings) and methods of calculation the level of permeability of oxygen, nitrogen and some gases in such systems. In terms of significant interest to the sensory properties of organic-inorganic systems, some theories, methods of application and techniques of analysis of reactions to environment change were proposed in [94, 178-184]. Even software for conversion of received signals into digital data was developed in [185]. Finally, the hybrid materials find their applications in industry and various types of equipment [186, 187].

The analysis of literature data showed the presence of significant interest to hybrid organic-inorganic polymer systems, in terms of prospects of their use in various spheres of human life and the possibility of implementation in industry due to their unique properties, which are inherent to both organic and inorganic components, and simplicity of regulating these properties.

New method of synthesis of hybrid organic-inorganic systems through joint polycondensation of organic and inorganic components that contain reactive groups, which was developed in the Institute of Macromolecular Chemistry of NAS of Ukraine, is very attractive from the technological point of view in comparison with popular multistage methods. Works focused on study of this method showed the possibility of synthesis of hybrid systems based on urethane oligomers and metal silicates, in which polymerization occured due to reactions between reactive free NCO-groups of the organic component and OH-groups of the inorganic component. Analysis of the literature showed the presence of many works devoted to chemism of such OIS, however, it was found that physicochemical properties of these hybrid systems and their relationships with the structure remained insufficiently investigated. Thus, the topic of the thesis is urgent in terms of comprehensive studies of properties (mechanical, thermal, electrical, etc.) and establishing the relationships between structure and properties of such hybrid systems.

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Synthesis and rheological behavior of hybrid organic-inorganic polymer systems

2.1. Introduction

2.2. Joint polycondensation and rheokinetic phenomena of hybrid organic-inorganic polymer systems

Chapter 2

Synthesis and rheological behavior of hybrid organic-inorganic polymer systems

2.1. Introduction

Organic-inorganic systems were synthesized in reactive mixture of organic (macrodiisocyanate MDI + poly(isocyanate) PIC) and inorganic component (sodium silicate SS) by their joint polycondensation. The rheological behavior of hybrid organic-inorganic systems was studied during their polymerization *in situ* using various rheokinetic methods. It was found that the concentration dependences of rheokinetic parameters, such as gelation time, rate constant etc., have the anomalous extreme character. It was explained by the effect of the simultaneous polymerization of two different types of hybrid organic-inorganic networks, which are characterized by different rate of structure formation, due to different reactivity of organic components.

2.2. Joint polycondensation and rheokinetic phenomena of hybrid organic-inorganic polymer systems

The extended description and the results of synthesis and rheological behavior are represented in the attached publication (Page 46).

The anomalous behavior of physical-chemical parameters during polymerization of organic-inorganic polymer systems based on reactive oligomers[1]

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Abstract

Dependencies of physical-chemical characteristics on structure development during polymerization of organic-inorganic systems (OISs) have been investigated. The non-monotonic tendency of changing of the physical parameters has been found. This effect was explained by complicated structure of OIS, which consists of two interpenetrating hybrid organic-inorganic networks, which are characterized by different rate of structure formation.

Keywords: *hybrid organic-inorganic systems, urethane oligomers, in situ polymerization, rheological properties, rheokinetic properties.*

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Submitted to e-polymer J.

1.Introduction

Organic-inorganic polymer systems (OISs) are new type of polymers, the large-scale investigations of their structure and properties started only over the last years. The study of OISs has attracted an attention of researches because of the possibility of obtaining a variety of properties owing to their chemical structure that includes organic and inorganic blocks in its volume (e.g. Sugimoto H. et al.[1], Sanchez C. et al. [2]). By investigations of electrical and dielectric properties of OISs the increase of relaxation time and activation energy with increasing of value of inorganic component has been shown (e.g. Li C. et al. [3]). The dependencies of electrical characteristics of OISs on structure of mineral blocks, chemical content and molecular weight of organic component, molecular structure of OISs have been investigated in (e.g. Bronstein L.M. et al. [4], Xi J. et al. [5], Kuo P-L. et al. [6], Mamunya Ye.P. et al. [7]). The content of mineral phase influences on thermal physical properties and thermal stability of OISs as it was illustrated in (e.g. Chen S. Et al. [8]).

The earlier studies of OISs (e.g. Mamunya Ye.P. et al. [9]) based on urethane oligomers and metal silicate made it clear that nature of organic phase appreciably influences on their electrical properties. With increasing of number of reactive NCO-groups in organic component the conductivity decreased for several decades, the dielectric constant and dielectric losses were changed drastically in wide range. Such systems can have a practical interest as the materials for fuel cells, rigid electrolytes, medicine and require the investigation of their structure forming features.

As usually, the changes of physical parameters during forming of structure of thermoset polymer systems have monotonic character (e.g. Lipatov Y.S. et al. [10]). With increasing the content of one of the components in a volume of polymer which is being formed, the values of kinetic parameters, such as rate constant, gelation time, curing time etc change consistently with the changes of physical properties of the system (e.g. Davidenko, V. V. et al. [11]). While organic-inorganic polymer systems (OIS) are a new class of polymers their properties and features of structure development are not investigated fully (e.g. Kickelbick G. et al. [12]). In the present work, the changes of physical-chemical parameters depending on structure formation were investigated.

2. Experimental

The organic component consists of a mixture of two isocyanate-containing products:

- preformed macrodiisocyanate (MDI) with *Mw* = 4500 which contains 3.6 % of free NCO-groups and is characterized by long chains. MDI was synthesized on the base of 2,4-toluene diisocyanate and oligooxypropylene-glycol with *Mw* = 2100.

- isocyanatecontaining modifier (IM) based on diphenylmethandiisocyanate (*Mw*=250) which is characterized by short chains with 32 % of free NCO-groups.

Inorganic component was Na-salt of polysiliceous acid (NS) existing in the form of oligomer in the water solution. Detailed characteristics of the products were given in (e.g. Mamunya Ye.P. et al. [18]).

Weight ratio of parts of organic component (MDI/IM) was varied in the range from 0/100 to 100/0, that enabled to change the content of the reactive NCO-groups in the range 3,6%-32% . The ratio organic/inorganic components (MDI+IM)/NS=70/30 was used for all cases.

Synthesis of OISs was fulfilled in reactive mixture of organic and inorganic oligomers, the reactions of synthesis were described in (e.g. Mamunya Ye.P. et al. [17]). The reactive mixture after 4 minutes of mixing was placed between two plates for rheokinetic and electrical measurements and on interdigitated electrode for dielectric investigations.

Representative kinetic characteristics (viscosity η and conductivity σ) were measured by a modified rheological equipment Reotest at temperature T=32^{0}C in which the cone plate elements were used as the electrodes for measuring of conductivity. This equipment was coupled with a teraohmmeter E6-13A Radiotechnika (Riga, Latvia) that allowed us to measure viscosity and conductivity simultaneously. The reactive mixture after 4 minutes of mixing was placed into cone plate elements with gap thickness of 200 μm. The speed of rotation was constant and equal to 3 min^{-1}, and the applied voltage equal to 100 V.

Rheokinetic parameters (G' and G'') were also determined by dynamic tests with a Rheometrics equipment RMS 800. The reactive mixture after 4 minutes of mixing was

placed between two plates with 11 mm in diameter. The thickness of the sample was 1 mm. A time sweep at temperature T=19^{0}C and constant shear frequency ω=1 rad s^{-1} was used to obtain the gelation time of OISs.

Dielectric characteristics during curing were investigated by dielectric analyser Solartron SI1260 at temperature T=22 ^{0}C in the range of frequency from 10^1 Hz to 10^6 Hz. The reactive mixture after 4 minutes of mixing was placed on interdigitated electrode IDEX Sensor with A/D ratio = 80 and a spacing of 125 μm.

3. Results and discussion

Fig. 1 presents the dependencies of viscosity η and electrical conductivity σ of OISs on time of polymerization. In accordance to (e.g. Madbouly S.A. et al. [13], Chambon F. et al. [14], Winter et al. [15]) reported that gelation time t_g can be determined as a critical conversion point of crosslinking reaction.

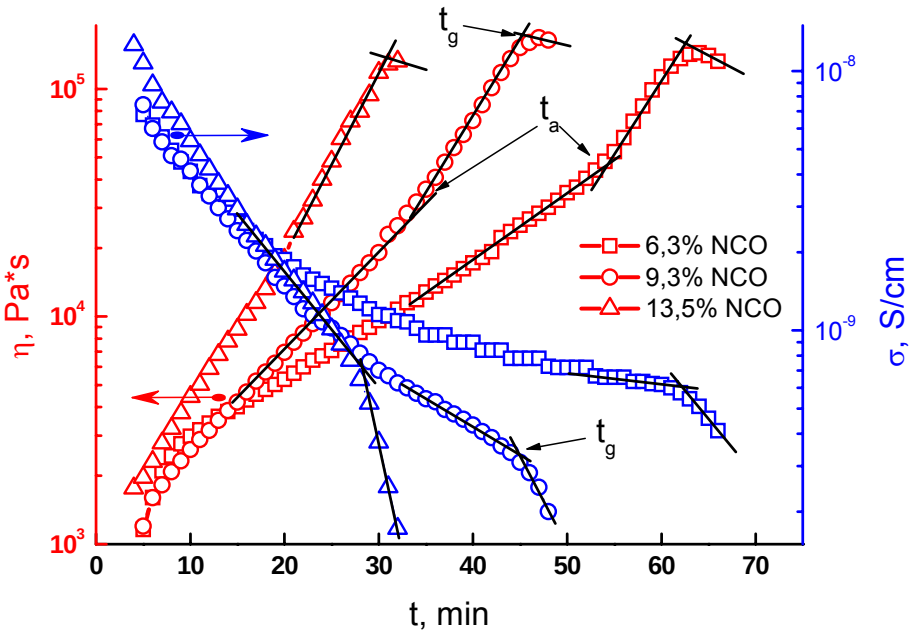

Fig. 1. The dependencies of η and σ of OISs on time of curing for systems with 6,3%, 9,3% and 13,5% of free NCO-groups

Gelation time t_g was defined on both viscosity and conductivity curves as a point of drastic changes of the curves shape as it is shown on Fig. 1. A good correlation between dependencies of viscosity and conductivity is observed, consequently it is possible to say, that the influence of chemical composition on structure development and the charge

transport has a similar character. The critical point t_a characterizes the transition from microgel formation to forming of macrogel (e.g. Zakordonskii V.P. et al. [16]).

Fig. 2 represents the dependencies of real G' and imaginary G'' parts of storage module on time. In our study we choose the crossover of G' and G'' as a gel point, that is a first approach of Winter-Chambon criterion (e.g. Madbouly S.A. et al. [13], Chambon F. et

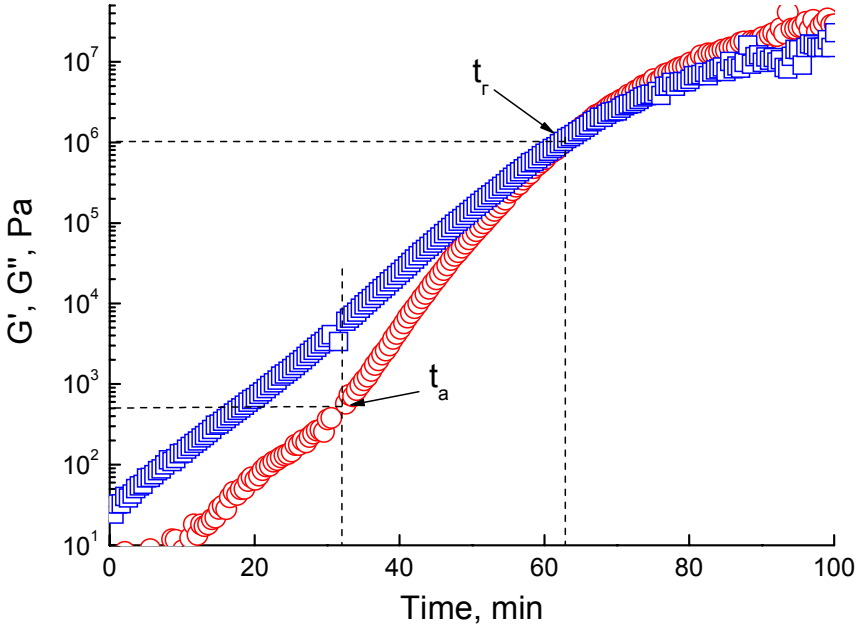

Fig. 2. The dependencies of G' and G'' on time curing of OISs with 17,8% of NCO-groups.

al. [14], Winter et al. [15]). One can see that the gelation time obtained by this method is longer than by critical point of crosslinking reaction (Fig. 1). This discrepancy was explained by the different methods of rheokinetic investigations and conditions of polymerization (temperature etc.).

A monotonic changing of physical parameters, which characterize the structure development, in accordance with continuous increasing of content of free NCO-groups from 3,6% to 32% in organic part and constant ratio 70/30 between organic and inorganic components, was expected.

Whereas, the experimental results, which were obtained during polymerization of OIS, demonstrate non-monotonic dependencies of kinetic parameters. Fig. 3 shows the influences of content of NCO-groups on gelation time t_g defined by viscosity, conductivity and G'/G'' crossover. Fig. 4 represents the dependencies of rate constant k on content of free NCO-groups in organic part of OISs.

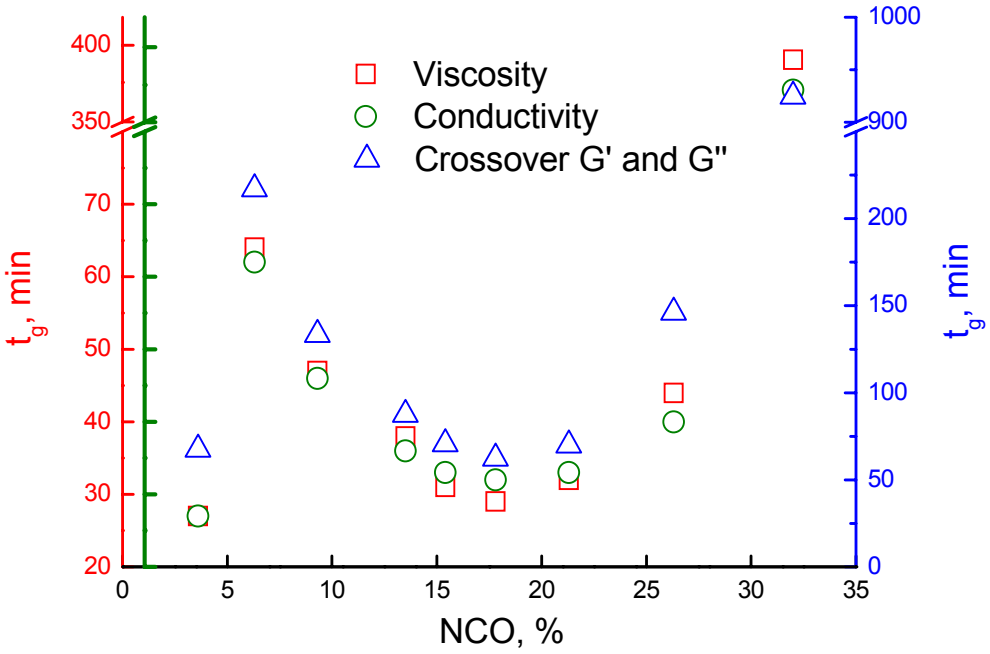

Fig. 3. Dependencies of gelation time on content of NCO-groups in OISs

The speed constants k were determined for the first linear areas of viscosity curves up to the critical point t_a on Fig. 1, which are corresponded to the microgel formation according to (e.g. Zakordonskii V.P. et al. [16]). As the figures indicate the curves have maximum or minimum in the mean concentration interval of NCO-groups. The same tendency has been found by dielectric measurements during polymerization of OISs.

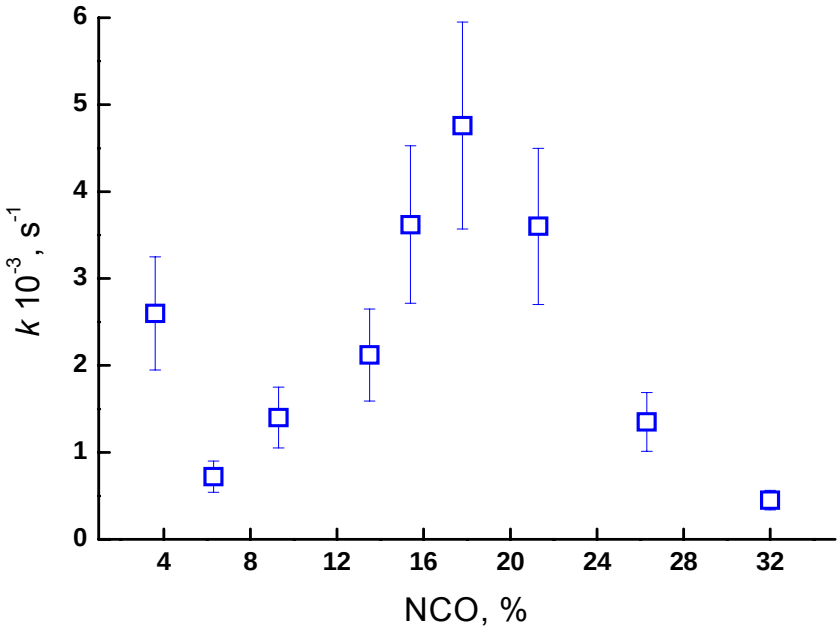

Fig. 4. Dependencies of rate constant on content of NCO-groups

Fig. 5 demonstrates the curves of relative permittivity $\varepsilon'/\varepsilon'_C$ versus content of NCO-groups (where ε'_C is permittivity of cured system) for 3 periods of curing. Evidently the results displayed on Fig. 5 show us that in these systems the reactions of curing run continually after t_g (see Fig. 3) i.e. take place the post-curing of OISs.

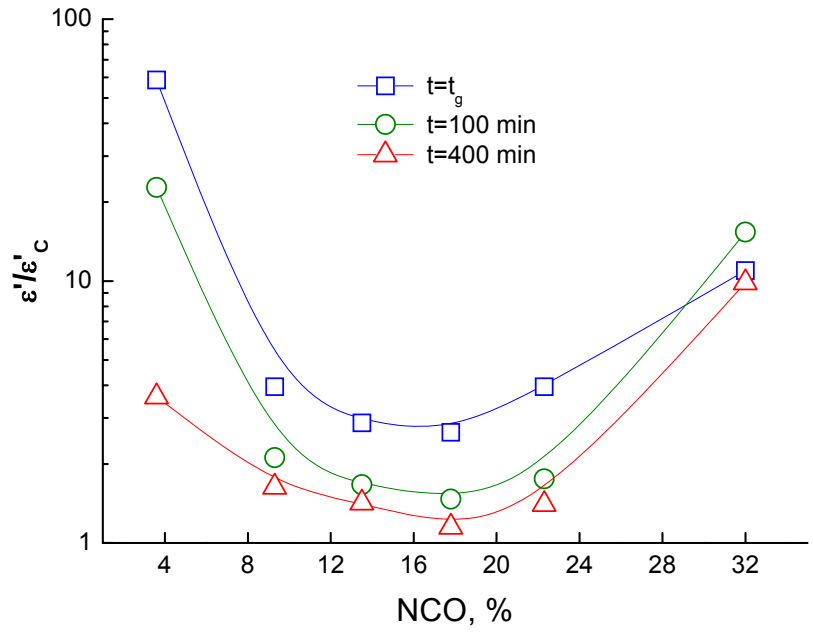

Fig. 5. Dependencies of relative permittivity (at 10^3 Hz) on content of NCO-groups during third stage of polymerization

As it is represented in (e.g. Mamunya Ye.P. et al. [17]) the polymerization of OISs has a complicated character and cannot be explained by one simple mechanism during all polymerization. On the other hand, the polymerization can be conditionally regarded as being in several continuous stages, which can be described by simple functions (e.g. Zakordonskii V.P. et al. [16]). In accordance to (e.g. Zakordonskii V.P. et al. [16]) the first stage of polymerization lies in kinetic interval, which is characterized by low increasing of viscosity, and describes the formation of chains. The second stage can be referred to the diffusion interval and is attributed the creation of aggregates or microgels.

This stage can be characterized by the sharp increase of viscosity with time of curing. The third stage is envisaged by creation of three-dimensional molecular structure and displays strong growth of viscosity. The presence of knee on the *G'* and *G''* curves (Fig. 2) is sourced by transition from second to third stage and is characterized by time t_a (Fig. 2). Third stage runs up to system gelation at time t_g.

As it is obvious from figure 1, the structure development of OISs excludes the presence of first stage of polymerization because of presence of long molecular chains in organic part which are used for OISs formation. The viscosity of systems begins to grow up in the moment of reactive mixture obtaining, due to fast reactions which run between free NCO-groups of organic component and OH-groups of inorganic component, and increases, due to growth of hybrid polymer network, until the gelation time t_g when the forming of structure is finishing and the post-curing of systems takes place.

The monotonic decreasing of gelation time t_g and increasing of reaction rate constant k for the systems with 3,6%-17,8% of NCO-groups occur due to increasing of content of reactive NCO-groups in reactive mixture. However with further increasing of NCO-groups the curves acquire the anomalous view. The gelation time begins to grow up, whereas the value of rate constant drastically falls down. The same tendency was also revealed for relative permittivity (Fig. 5). Such anomalous dependencies are difficult to describe by one simple mechanism. They can be explained by complicated character of interphase interaction between organic and inorganic components during polymerization of OISs. In the low concentration interval of NCO-groups, when relatively high-molecular macrodiisocyanate (MDI) is dominate in organic part, the hybrid organic-inorganic network MDI-Na-salt of polysiliceous acid (NS) is formed in the volume of composite, whereas hybrid organic-inorganic network isocyanatecontaining modifier (IM)-NS is created in the boundary area nearby surface of inorganic phase (Fig. 6).

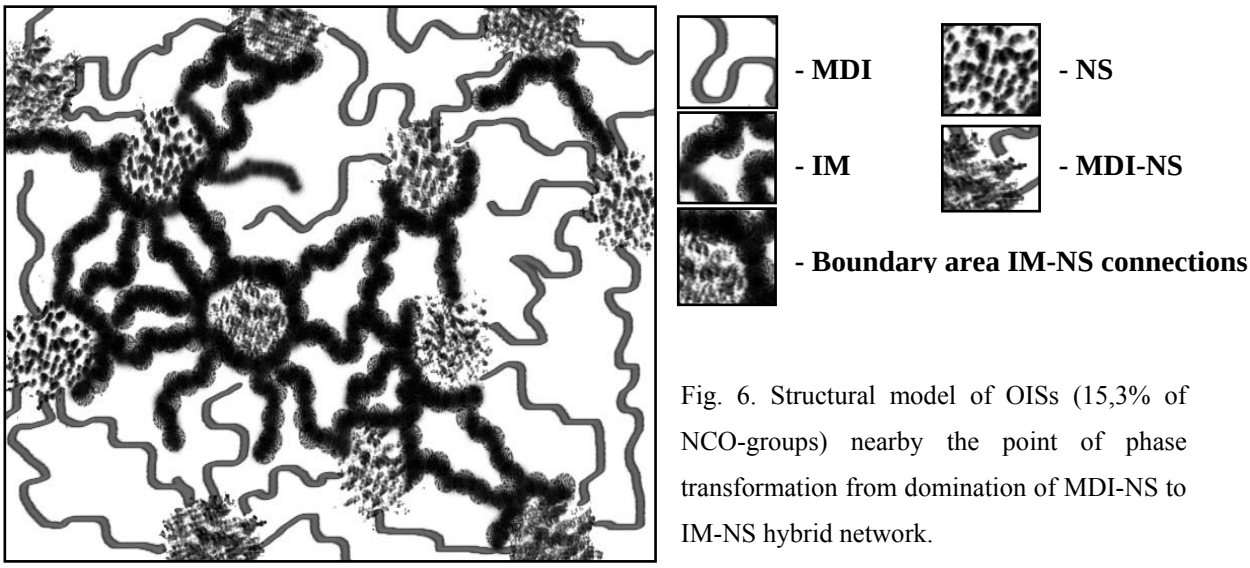

Fig. 6. Structural model of OISs (15,3% of NCO-groups) nearby the point of phase transformation from domination of MDI-NS to IM-NS hybrid network.

Such difference between two hybrid networks is due to different molecular weight of MDI and IM and consequently the different mobility of their chains and different rate of reactions MDI-NS and IM-NS. In the interval of content of NCO-groups from 17,8% to 32% the hybrid organic-inorganic network IM-NS becomes predominate and forms the layer around the inorganic phase, which prevents to the following reactions between organic and inorganic phases.

Thus, two hybrid organic-inorganic networks were obtained in OISs, which are characterized by different structures and properties correspondingly, that explains a such anomalous behavior of kinetic parameters during the polymerization.

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Thermomechanical behavior of hybrid organic-inorganic polymer systems Structural model

3.1. Introduction

3.2. Mechanical properties of hybrid organic-inorganic polymer systems

3.3. Thermomechanical properties of hybrid organic-inorganic polymer systems

Chapter 3

Thermomechanical behavior of hybrid organic-inorganic polymer systems. Structural model

3.1. Introduction

The mechanical and thermomechanical properties of the synthesized hybrid organic-inorganic systems were studied using TMA methods, creep/relaxation and stess/strain tests. It was revealed that two types of hybrid organic-inorganic networks that exist in the bulk of synthesized hybrid systems are characterized by various mechanical and thermomechanical properties. First hybrid network is elastic and weekly cross-linked (T_g≈-40 ^{o}C), while the second is rigid and highly cross-linked (T_g >> room temperature) because of difference in the chemical structure of organic components. When the elastic hybrid network is dominant in the bulk of organic-inorganic system, the second hybrid network exists in the form of domains in its matrix and general properties of hybrid systems are prevalently determined by the properties of elastic hybrid network. In the case of dominance of rigid hybrid network, general properties of hybrid systems are prevalently defined by its properties, while the elastic hybrid network has insignificant effect. On the basis of the obtained results the structural model of hybrid organic-inorganic systems is proposed.

3.2. Mechanical properties of hybrid organic-inorganic polymer systems

The extended description and the results of mechanical investigations of hybrid organic-inorganic systems are represented in the attached publication (Page 58).

3.3. Thermomechanical properties of hybrid organic-inorganic polymer systems

The extended description and the results of thermomechanical investigations of hybrid organic-inorganic systems are represented in the attached publication (Page 74). Also, the introduced results are compared with the results of dielectric and electrical invstigations of these hybrid systems.

Mechanical properties of organic-inorganic polymer systems based on urethane oligomers[2]

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Abstract

The dependencies of creep and mechanical relaxation, elongation and stress/strain function, elasticity modulus at elongation and pressure on the chemical composition of organic component of OIS based on oligoetherurethane, polyisocyanate with low molecular weight, and metal silicate were investigated. A good correlation between changes of mechanical parameters and structure of hybrid organic-inorganic network, which is formed during synthesis of OIS have been established.

Keywords: hybrid organic-inorganic systems, urethane oligomers, in situ polymerization, mechanical properties, creep, relaxation, stress/strain, elasticity.

[2] Printed in Ukr. Polym. J. 31 (2009) 51-57
Submitted to J. of Non-Cryst. Sol.

1. Introduction

Organic-inorganic polymer systems (OIS) is a new class of polymers, which large-scale structure and properties studies started relatively recently. The reason of the interest to these systems is the possibility of their chemical structure variation, which includes organic and inorganic blocks, which in turn makes it possible to change the properties of OIS in a wide range and to obtain materials with necessary characteristics.

Today the most popular way of OIS obtaining is sol-gel method, which is effective for the synthesis of hybrid organic-inorganic systems with specified properties.Thus, the possibility of multifunctional organic-inorganic systems designing using sol-gel technology by changing the chemical composition and structure of inorganic phase was considered in [1]. However, this way is multistage and rather difficult. The original method of OIS synthesis by joint polymerization of liquid reactive organic and inorganic oligomers has been proposed in [2, 3]. The structure of such OIS is an organic polymer matrix with inorganic phase inclusions, the inclusion of these are from nanometer dimensions, namely the order 7-10 nm [4], to several tens of micrometers. This structure provides the special electrical, dielectric and other properties of OIS.

Studying the electrical and dielectric properties of OIS authors [5] showed the increasing of the relaxation time and activation energy with content increasing of inorganic component. The content of inorganic phase also affects on the thermal properties and thermostability of OIS [6,7]. The dependences of electrical parameters on the OIS inorganic building block, chemical composition and molecular weight of organic component and molecular structure of OIS were determined in [8-11].

Previous studies of OIS based on urethane oligomers and metal silicate showed that the chemical composition of organic phase significantly affects on their electrical properties, while increasing the number of reactive NCO-groups in the organic component decreased the conductivity more than two decades and changed the permittivity and dielectric losses in a wide range [12]. Such systems has a practical interest and can be used as the coatings, solid electrolytes and materials for medical purposes, which require investigation of their mechanical characteristics.

The purpose of this work was to establish the dependences of mechanical properties - creep (deformation of the material in time under the action of constant load) and stress relaxation (change of sample deformation during unloading) and limiting characteristics at break (elongation and efforts at destruction of the sample) on chemical composition of OIS organic component based on isocyanate-containing oligoetherurethane, low-molecular polyisocyanate and metal silicate. Results were described by a theoretical justification based on Burger's four-element mechanical model.

2. Experimental

2.1. Materials

OIS were synthesized in the reactive mixture of organic component, which had free reactive NCO-groups and the inorganic component with reactive OH-groups. The organic component consists of oligoetherurethane (UO) - macrodiisocyanate with Mw = 4500 and 3,6% of NCO-groups, which was synthesized on 2,4 and 2,6-toluenediisocyanate (TDI 80/20) and oligooxypropyleneglycol with molecular weight 2100, and low-molecular polyisocyanate with Mw = 250 and 32% of free NCO-groups (PIC). The ratio UO/ PIC was varied, the total number of NCO-groups in the organic component was calculated from additive contributions of components. The inorganic component was metal silicate (MS), which exists in the form of oligomer [13]. The ratio of organic/inorganic components was equal to 70/30 for all OIS. Detailed reactions of OIS polymerization are described in [4, 14]. The reactive mixture was carefully mixed until the complete homogenization state, placed in teflon form with appropriate configuration (in the form of blades for break tests, or in the form of disks for creep measurements), in which the OIS curing was procceded at room temperature (22 ± 1 ^{o}C) during 24 hours.

2.2. Equipment

Creep and stress relaxation investigations were done using the original equipment in compression mode with the load force equal to 0,057 MPa. OIS samples with 12 mm in diameter and a thickness of 1,5 mm were loaded up using the flat-end indentor with 3 mm in diameter. Load time was taken 5 minutes with the measuring frequency 0,5 s^{-1}. Further the force was unloaded and the stress relaxation was determined during next 5 minutes.

Elongation experiments and efforts at mechanical destruction were fulfilled by the discontinuous machine 2166 P-5 at a stretch rate of 50 mm/min.

3. Theoretical model

3.1. Creep and relaxation

The simplest model, which describes the stress relaxation is Maxwell's two-element model [15, 16], but its usage for mechanical deformation in polymer and composite systems interpretation leads to significant discrepancies with experimental results. In this paper to describe the experimental creep and stress relaxation curves Burger's four-element viscoelastic model was used. This model is a combination of elastic elements (springs) with the Hookean deformation and dampers, which are deformed according to Newton's law [15, 17, 18] (Fig.1-a). Theoretical creep and stress relaxation curves of Burger's model are shown in Fig. 1-b.

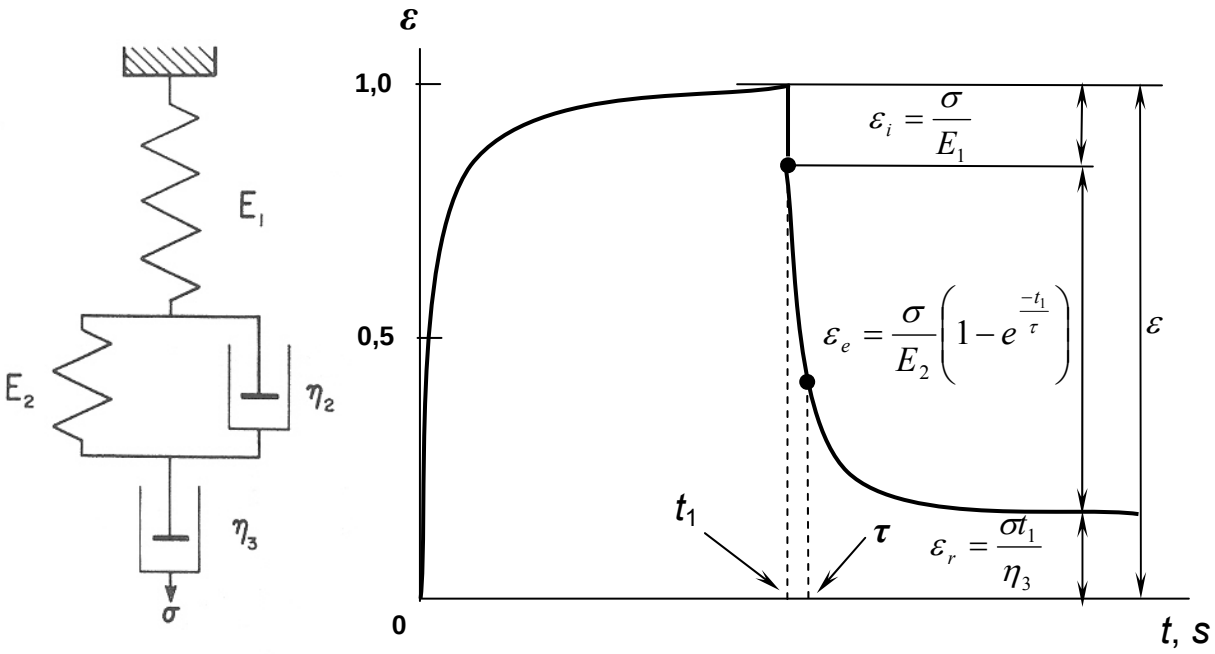

Fig. 1-a. Burger's four-element theoretical model

Fig. 1-b. Theoretical creep and stress relaxation curves of Burger's model.

Overall, in line with this model the deformation in time under the constant load can be divided into three successive stages: the instantaneous deformation, primary creep and static creep [17, 19]. According to [15], the full deformation of the system ε is the sum of three types of deformation: instantaneous deformation $\boldsymbol{\varepsilon_i = \sigma/E1}$, elastic deformation $\boldsymbol{\varepsilon_e=\sigma/E_2[1-exp(-E_2t/\eta_2)]}$, and plastic (residual) deformation $\boldsymbol{\varepsilon_r = \sigma t/\eta_3}$ (which is Newtonian flow). It can be described by the following equation:

$$\varepsilon = \varepsilon_i + \varepsilon_e + \varepsilon_r = \frac{\sigma}{E_1} + \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{E_2 t}{\eta_2}\right)\right] + \frac{\sigma t}{\eta_3} \qquad (1)$$

where E_1 and E_2 are modulus of elasticity of elastic elements, η_1 and η_2 - the viscosity of liquids in dampers, σ - load force and t - creep time.

At the load moment the initial deformation of the system is only equal to the instantaneous deformation ε_i of the spring E_1. Further strain ε_e is due to the creep of the system, ie, spring E_2 deformation and damper η_2 displacement, as well as damper η_3 displacement, which is responsible for residual deformation ε_r.

After unloading the strain recovery, namely stress relaxation, can be described by the equation (2) similar to the equation (1):

$$\varepsilon = \frac{\sigma}{E_1} + \varepsilon_e\left[\exp\left(-\frac{t - t_1}{\tau}\right)\right] + \frac{\sigma t_1}{\eta_3} \qquad (2)$$

where

$$\varepsilon_e = \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{t_1}{\tau}\right)\right]$$

In this equation the value of $\boldsymbol{\tau = \eta_2/E_2}$ is defined as the stress relaxation time. At the unload moment the strain $\varepsilon_i = \sigma/E_1$ is momentary recovered and does not take a part in the system relaxation. The recovery of the deformation occurs except damper η_3 displacement, the residual deformation $\boldsymbol{\varepsilon_r = \sigma t_1/\eta_3}$ remains. Thus, the stress relaxation corresponds to elastic deformation ε_e only:

$$\varepsilon_e = \frac{\sigma}{E_2}\left[1 - \exp\left(-\frac{t_1}{\tau}\right)\right] \qquad (3)$$

where t_1 - the initial moment of the elastic strain relaxation after the instantaneous strain ε_i recovery. The stress relaxation time τ can be experimentally determined from the equation (4):

$$\frac{\varepsilon}{\varepsilon_e} = e^{-\frac{t-t_1}{\tau}} \qquad (4)$$

The ratio $\boldsymbol{\varepsilon/\varepsilon_e = e^{-1} = 0{,}368}$ corresponds to the time $\boldsymbol{t-t_1 = \tau}$, ie to the stress relaxation time value (Fig. 1-b).

Modulus of elasticity

Dependencies stress/strain allow to calculate an elastic modulus E, under the conditions that Hooke's law is performed at small deformations:

$$\sigma = \varepsilon E$$

The initial linear region tilt of the stress/strain dependence characterizes the modulus of elasticity, which is Young's modulus for elongation:

$$E = \frac{d\sigma}{d\varepsilon} = \frac{F}{(L - L_0)/L_0} \qquad (5)$$

where F – is the strain, L_0 – the initial sample length, L – the length of the sample deformed under the load. For the case of deformation in compression mode the modulus of elasticity is calculated the same way, while F indicates the pressure on the sample, and the relative deformation ε equals to $\boldsymbol{(L_0-L)/L_0}$.

4. Experiment results

Fig.2 represents dependencies of the creep under the constant stress equals to 0,057 MPa, and the stress relaxation after unloading on time for samples with 3,6%, 13,5% and 26,1% content of NCO-groups. The calculated curves of deformation under the load and the stress relaxation of OIS with 3,6% of NCO-groups are shown. .Apparently, there is good correspondence between experimental (points) and calculated (lines) values. A good correlation between experiment and calculation was also found for all OIS.

The values of complex deformation ε and its components (instantaneous deformation ε_i, elastic deformation ε_e and residual deformation ε_r) are also marked in the full size figure. Apparently, OIS have rather high residual deformation ε_r, while instantaneous deformation ε_i, calculated as $\boldsymbol{\varepsilon_i = \varepsilon - \varepsilon_e - \varepsilon_r}$, gives a low contribution in the total strain comparing to ε_e and ε_r.

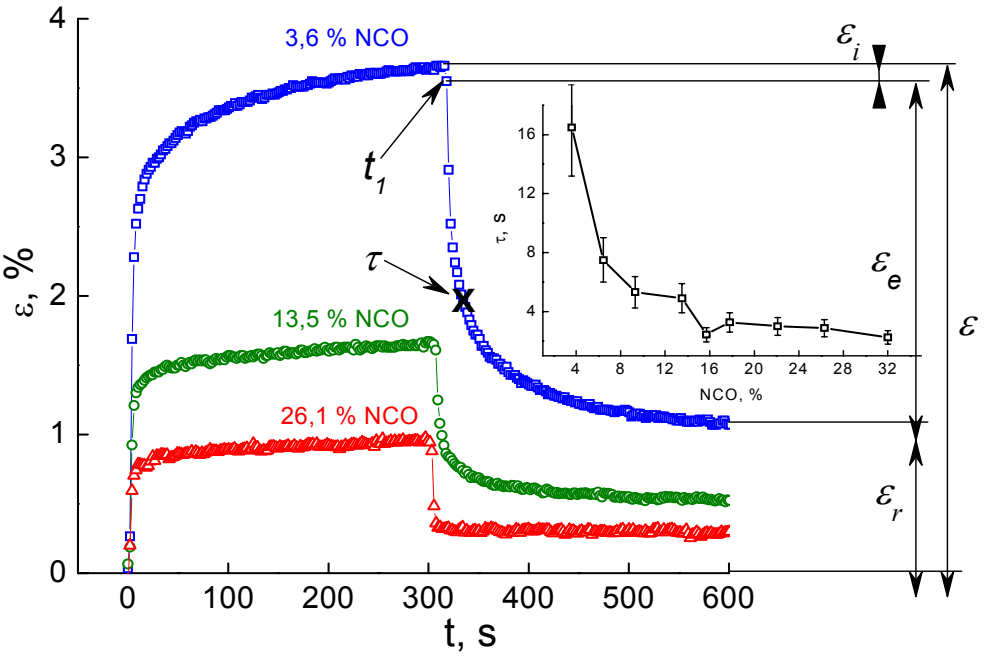

Fig. 2. Dependencies of creep and stress relaxation on time for samples with different content of NCO-groups. In the insert the dependence of stress relaxation time τ on the content of NCO-groups is provided.

The figure also represents the time t_1 and the stress relaxation time $\boldsymbol{\tau = t - t_1}$. Evidently, the stress relaxation time is much shorter than the measurements period. The dependence of stress relaxation time τ on content of NCO-groups is provided in the insert of the figure. From this dependence follows that the stress relaxation time decreases rapidly with increasing the number of NCO-groups and reaches a constant value in the interval 15,3-32%.

Fig. 3 shows dependences of complex ε, elastic ε_e, residual ε_r and instantaneous deformation ε_i on the content of NCO-groups.

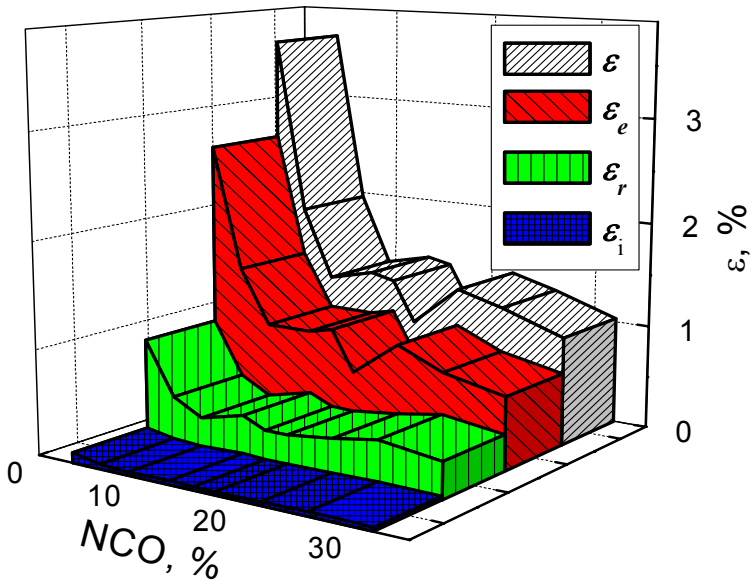

Fig. 3. Dependencies of of complex ε, elastic ε_e, residual ε_r and instantaneous deformation ε_i on the content of NCO-groups.

Apparently, all deformations rapidly decrease for OIS with the small content of NCO-groups and purchase almost constant values for the content of NCO-groups higher than 15.3%. The main contribution into the complex deformation ε is given by elastic ε_e and residual ε_r deformations, while the influence of instantaneous deformation ε_i is negligible.

Stress/strain dependencies during elongation until the break of OIS containing 3.6%, 6.3%, 9.3% and 22.3% of free NCO-groups are represented in Fig. 4. One can see that the ability to strain sharply decreases with increasing of the NCO-groups content, while the load required for OIS mechanical distruction increases. As the figure indicates the sample with 3,6% of NCO-groups is characterized by the high value of relative strain (ε = 1200%) and low value of breaking load (σ = 1,0 MPa). Contrariwise, the composition containing 22,3% of NCO-groups of is specified by the low value of relative elongation (ε = 10%), with the high value of breaking load (σ = 22,0 MPa). The concentration curve of the relative deformation ε at elongation is shown in the insert of the figure. The direction of this parameter changing coincides with the dependencies of parameters calculated at compression. At low concentrations of NCO-groups the strain value rapidly decreases (more than two decades) and becomes insignificant when reaching 15,3% of NCO-groups.

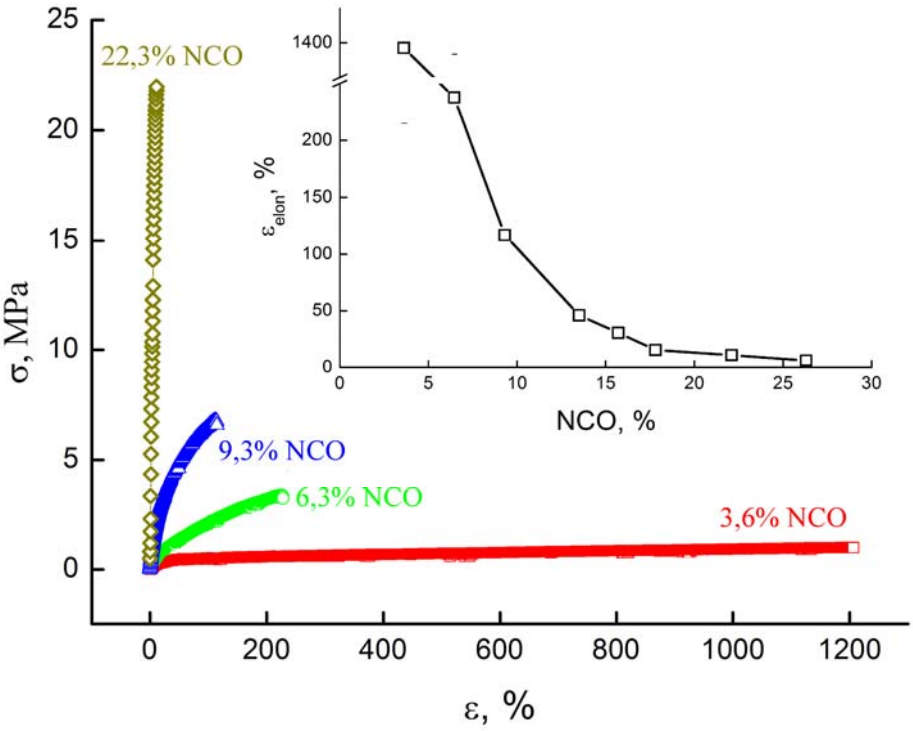

Fig. 4. Stress/strain dependencies during elongation of OIS with different content of NCO-groups.

Fig.5 shows the dependencies of Young's modulus at elongation and compression on the content of NCO-groups. In the region of small as well as high values of the content of

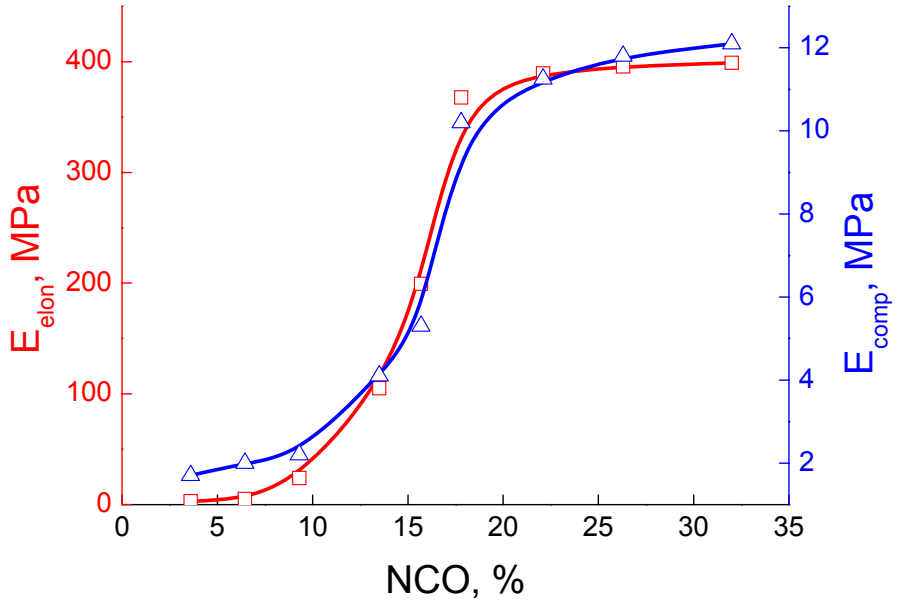

Fig. 5. Dependencies of Young's modulus at elongation E_{elon} and compression E_{comp} on the content of NCO-groups.

NCO-groups Young's modulus remain constant, while in the range 13-17% of NCO-groups rapidly change their values.

5. Discussion of results

Previuosly the structural model of this OIS type was proposed in [12], which describes the presence of two hybrid organic-inorganic networks with different crosslinks density and molecular mobility. The first network is elastic with higher molecular weight of the segment between the network nodes and high mobility, which is formed by the reaction of the organic compound component - oligoetherurethane UO (with a number of NCO-end-groups 3,6% and molecular weight equal to 4500) and inorganic component – metal silicate (MS). The second network is rigid and appears as the result of interactions between the second part of the organic component - polyisocyanate PIC (with 32% of NCO-groups and molecular weight equal to 250) with MS. This network has a shorter molecular segment and, consequently, low mobility. The variation of the content of free NCO-groups in the composition organic component gives the opportunity to obtaine hybrid systems with different ratio of rigid and elastic hybrid networks, which determines the total mechanical properties of OIS.

This general model can be developed more detail. Fig.6 shows the evolution of the structure by variation of the ratio of constituents UO/PIC in OIS organic phase, which explains the change of mechanical characteristics. In a system with a ratio UO/PIC = 1/0, which, respectively, contains 3,6% of NCO-groups, only the elastic hybrid organic-inorganic network UO/MS exists (Fig. 6-a). This network is characterized by the high strain ε, long stress relaxation time τ (Fig.2) and high deformation value at elongation (Fig. 4). The low-molecular PIC infusion into OIS organic part increases the number of reactive NCO-groups and leads to a second rigid hybrid organic-inorganic network appearance in the reaction of PIC and MS, which is formed as domains in the prevailing elastic hybrid network volume (Fig.6-b). These inclusion limit the mobility of the elastic network and lead to the reduction in deformation and relaxation time. Further increasing the content of NCO-groups develops more extensive rigid hybrid network and leads to the formation of two interpenetrating hybrid networks in the volume of OIS with 15-17% of NCO-groups (Fig. 6-c). In this content interval the deformative and relaxation properties of OIS are significantly reduced (Fig. 2, 4).

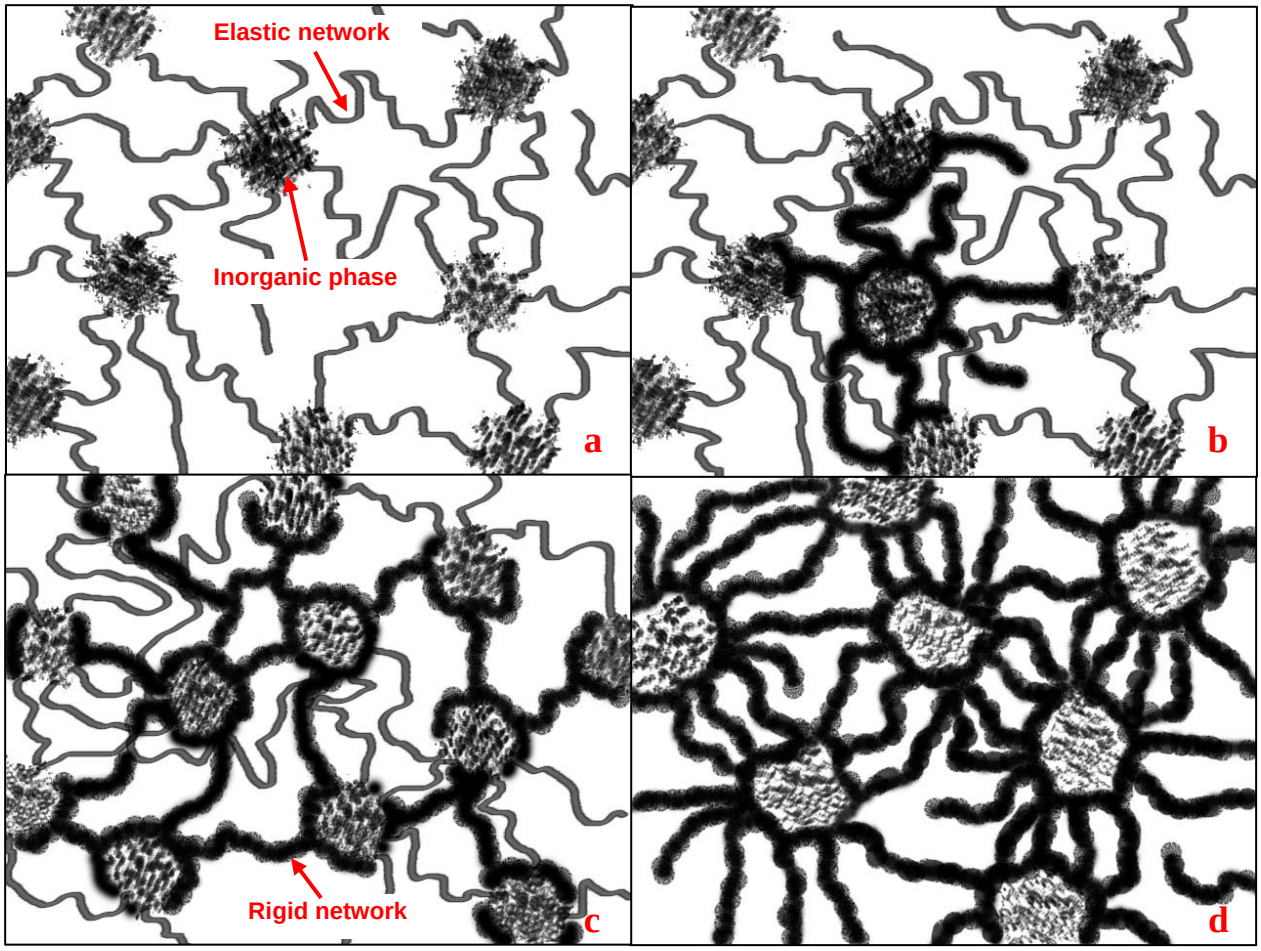

Fig. 6. OIS structural model: the evolution of the structure by variation of the ratio UO/PIC in OIS organic phase and, consequently, changing the number of NCO-groups.

With reaching 17,8% of NCO-groups the hybrid rigid network becomes dominant with elastic network inclusions, ie a phase inversion takes a place. Strain and the relaxation time values become constant, because the contribution of elastic network inclusions in deformative characteristics is negligible, so mechanical parameters of OIS are mainly determined by the influence of the rigid network. When the ratio UO/PIC = 0/1, which gives 32% of the content of NCO-groups in the organic component, only a rigid network is formed in the reaction of PIC and MS (Fig. 6-d).

Strees/starin depndenicies (Fig. 2) reflect this structure evolution with the changing of the NCO-groups concentration in the organic phase of OIS. It is clear that the total strain ε decreases with increasing of NCO-groups, ie with increasing the contribution of rigid network.Values of elastic ε_e and residual ε_r deformations reduced respectively. The change of stress relaxation time depending on the structure evolution is shown in the insert of the figure.

The rise of the rigid network inclusions in OIS with a dominant elastic network leads to a sharp decrease of the stress relaxation time, meanwhile, when the rigid network becomes dominant, the influence of the elastic network inclusions on the stress relaxation time is minor.

Fig. 3 represents the relations between the elastic, residual and instantaneous deformations. As noted earlier, the contribution of instantaneous deformation is insignificant. On the other hand, the contribution of residual (plastic) deformation increases slightly during the transition from elastic to rigid systems. Thus, the ratio of $\varepsilon_r/\varepsilon$, which shows the contribution of plastic deformation in total deformation, increases from 0,24 at 3,6% NCO-groups to 0,34 at 32% NCO-groups, ie the elastic network has better elastic properties. Literature data show that the contribution of elastic deformation in total deformation essentially depends on the composition of OIS. Thus, it was shown that OIS containing 20% of glass has a value of $\varepsilon_r/\varepsilon$ = 0,23 compared to $\varepsilon_r/\varepsilon$ = 0,56 for pure LDPE by the creep/relaxation investigations of organic-inorganic systems based on LDPE and tin-based polyphosphate glass (Pglass) [17]. Pretreating the Pglass with coupling agents leads to higher reduction of the residual deformation contribution, $\varepsilon_r/\varepsilon$ = 0,15 for OIS with 20% of phosphate glass treated with octadecylsilane. This significantly reduced the level of total deformation from 2,3% for LDPE to 0,18% for OIS with 20% for pretreared as well as for not pretreared glass. Thus, a rigid mineral phase decreases the level of common deformation and, at the same time, reduces the contribution of plastic deformation, ie elastic deformation becomes prevailing.

In our case the content of the mineral phase remained constant, but the composition of organic phase was changed, which led to changes in mechanical properties due to the formation of specific structure with two hybrid organic-inorganic networks. Total deformative characteristics were varied in a wide range (especially at elongation), but the contribution of plastic deformation remained significant. Maybe it can be explained by the presence of secondary low-molecular products of organic-inorganic reactions, which play the role of plasticizers, as the OIS polymerization is very complicated proccess with several parallel and consecutive reactions [14].

It should be noted that in the literature data devoted to studies of OIS obtained by sol-gel method the OIS structure considered as interpenetrating organic and inorganic networks [20-24]. Such networks can be generally divided into two classes, namely interpenetrating

networks with weak interfacial interactions due to the existence of van der Waals forces, hydrogen or coordination connetcions (class I of hybrid materials) [21]. Class II of hybrid materials is indicated by the strong interaction between organic and inorganic networks due to the formation of covalent linkages. The OIS structure we investigated does not charged of this simple classification and differs by the presence of two hybrid organic-inorganic networks with different organic chain length and, consequently, different mechanical properties.

Strain modulus at elongation E_{elon} and compression E_{comp} demonstrate different character depending on the content of NCO-groups in linear Hookean deformation area (Fig. 5). In the region of low as well as high values of NCO-groups, when the structure constists of dominant elastic network with rigid network inclusions or dominant rigid network with elastic network inclusions, the values of modulus is almost constant. Thus, inclusions does not give a significant contribution to the deformative properties of the polymer matrix for small levels of the strain (Hookean deformation). In the phase inversion region, which corresponds to the average content of NCO-groups, modulus values increase indicating the sensitivity of this parameter to the contribution of two interpenetrating networks. Such dependency nature confirms the rightness of structural model as elastic or rigid matrix with inclusions of the network with opposite properties, and not in the form of two interpenetrating networks across the range of NCO-groups concentrations.

6. Conclusions

Thus for OIS, in which the chemical structure of organic phase was changed, namely the ration of low-molecular PIC and isocyanate-containing oligoetherurethane UO was varied and the number of NCO-groups was consequently changed, the the structural model,which describes the formation of structure in the form of elastic organic-inorganic network UO-MS with rigid network inclusions or as a rigid organic-inorganic network PIC-MS with elastic network inclusions was proposed. The phase inversion occurs in the average content of NCO-groups due to the existence of two interpenetrating networks. Mechanical properties of OIS reflect these structural changes. In OIS with the prevailing elastic network the values of mechanical parameters decrease rapidly with increasing the content of NCO-groups and, accordingly, growing of rigid network inclusions. When the rigid network becomes prevailing the elastic inclusion gives an insignificant contribution into the deformative

properties of OIS. Modulus of elasticity are determined only by elastic properties of the dominant network, while the affect of other network inclusions is negligible.

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Thermomechanical and electrical properties of hybrid organic-inorganic polymer systems based on isocyanate-containing oligomers[3]

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Abstract

In the reaction of the organic oligomer (macrodiisocyanate+polyisocyanate), which has free NCO-groups, with the sodium silicate (SS) hybrid organic-inorganic systems (OIS) have been obtained. The structure of OIS represents the system with two interpenetrated hybrid networks: elastic network MDI-SS and rigid network PIC-SS. Depending on composition of OIS one of the networks is predominant and makes the continuous structure with the penetrated additions of the another network. Their electrical and dielectric properties (σ, ε' ma tan δ) rather different: the MDI-SS network is characterized by high values of conductivity, dielectric constant and tan δ, whereas the PIC-SS network has much lower values of this parameters.

Keywords: *hybrid organic-inorganic systems, urethane oligomers, in situ polymerization, thermomechanical properties, thermal stability, conductivity, permittivity.*

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1. Introduction

During the last years an intensive research of a new class of polymer materials - hybrid organic-inorganic polymer systems (OIS) has been begun. An interest is due to the OIS availability with a wide range of properties that can be sent to adjust and get materials with predetermined characteristics [1, 2]. For example, it can be materials with high ionic conductivity, synthesized by sol-gel method, and intended for use as solid electrolytes. [3, 4]. Also it can be OIS with high chemical and radiation resistance [5] and thermostability [6]. Some organic-inorganic systems may have a wide range of electrical, dielectric [7,8,9] and sorption properties [7, 8], depending on their composition.

Nowadays the most widespread way of OIS obtaining is sol-gel method [1, 3, 10], which is effective for the synthesis of hybrid organic-inorganic systems with defined properties. However, it is sequential and rather difficult process. The original method of OIS synthesis by joint polymerization of liquid reactive organic and inorganic oligomers has been proposed in [11-13]. By changing the chemical composition of organic/inorganic oligomers and their ratio the final product with properties varying in wide range can be obtained.

In the present work hybrid organic-inorganic polymer systems, obtained in reactions of organic (a mixture of macrodiisocyanate and polyisocyanate) and inorganic oligomers (sodium silicate) have been studied. Using a mixture of macrodiisocyanate and polyisocyanate gives the opportunity to vary the content of free NCO-groups in the organic component and change OIS structure, consequently. Thermomechanical, dielectric and electrical characteristics of OIS in a wide temperature range depending on OIS composition have been investigated.

2. Experimental

2.1. Materials and synthesis

The organic component was presented as a mixture of two products: urethane oligomer - macrodiisocyanate (MDI), which contained 3,6% of free NCO-groups and polyisocyanate (PIC) with 32% of free NCO-groups. Urethane oligomer was synthesized

on 2,4 and 2,6-toluenediisocyanate (TDI 80/20) and oligooxypropyleneglycol with molecular weight 2100. Polyisocyanate mark D was used.

The inorganic component of the compositions was sodium silicate (SS), which exists in oligomeric form in aqueous solutions with general formula

$$aNa_2O \bullet bSiO_2 \bullet cH_20$$

where *b/a* - silicate module, *c/a* - water ratio.

The industrial sodium silicate, which corresponds to National Standard GOST 13078-81, had next parameters: silicate module – 2,8, density – 1,45 g/cm^3.

OIS synthesis passed in the reactive mixture of organic and inorganic oligomers. The full description of OIS synthesis represented in [11-13]. After intensive mixing the reactive mixture was placed in a teflon form, where the product curing proceeded at room temperature (25 ± 1 ^{0} C) during 24 hours. Mass ratio of organic component's products MDI/PIC was varied within 0-100%, the ratio between organic and inorganic components has been taken beyond 70/30.

2.2. Equipment and measurement

Dielectric characteristics (permittivity ε′ and dielectric losses tg δ) were measured by ac bridge P5083 at a frequency of 1000 Hz. The conductivity (σ) on DC was determined using teraometr E6-13A.

Thermomechanical investigations were conducted using the original equipment in the penetration mode with the force F = 10 kg/cm^2. The temperature range, in which experiments were fulfilled, was -120 - 350 ^{o}C with a linear heating rate 3 ^{o}C/min.

Electrical studies were conducted on samples in the form of washers with 30 mm in diameter and a thickness of 1,5 mm. For thermomechanical experimants samples with 12 mm in diameter and a thickness of 1 mm were used.

3. Experiment results

3.1. Thermomechanical studies

Fig.1 shows the general thermomechanical curve (the dependence of relative sample deformation L on the temperature T) of OIS with organic components MDI/PIC ratio equal to 90/10, which corresponds to the content of NCO-groups = 6,45%. The relative strain L,% was determined from the equation:

$$L = \frac{\Delta L}{L_0} \cdot 100$$

where ΔL – sample deformation in microns; L_0 - initial sample thickness in microns.

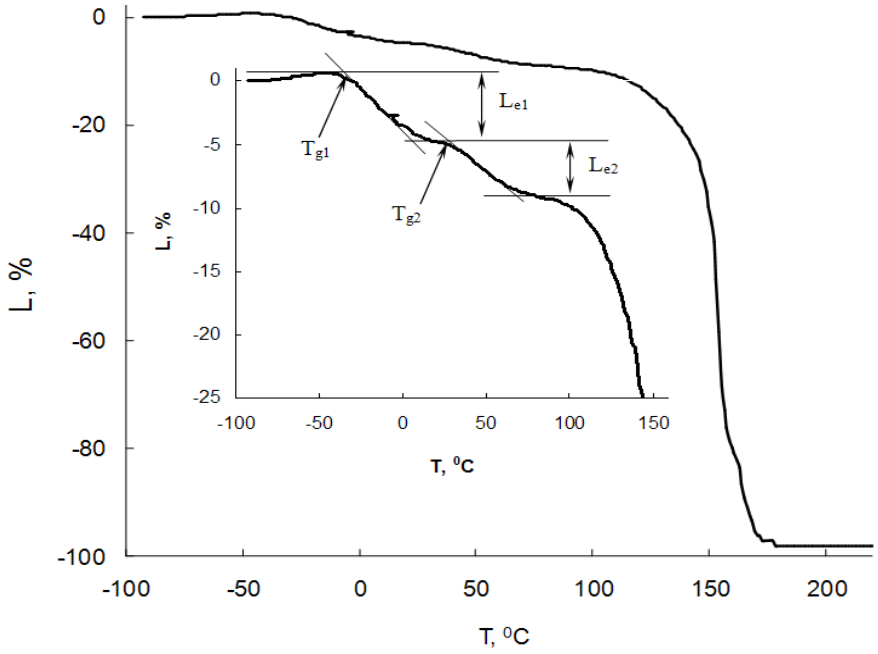

Fig. 1. The thermomechanical curve of OIS with organic component's products ratio MDI/PIC = 90/10, content of NCO-groups = 6,45 %.

In the insert of Fig. 1 the multiplied view of this curve for smaller deformation value is given (25%). As one can see, two areas of elastic deformation exist on the curve due to OIS structure transition from the vitreous to high elastic state. The presence of two transition regions indicates the existence of two glass transition temperature T_{g1} and T_{g2}. The temperatures of glass transitions were defined by two lines crossing, as it is shown in the insert of Fig. 1. The relative elastic deformation L_{e1} and L_{e2}, which correspond to the two structure transitions, were determined from the same curve. Values of T_g and L_e are

given in the table. From represented results follows that OIS structure contains at least two structural formations, which are characterized by different levels of the molecular mobility.

MDI/PIC	NCO, %	T_{g1}, ^{0}C	T_{g2}, ^{0}C	L_{e1}, %	L_{e2}, %
100/0	3,6	-40	-	15	-
90/10	6,45	-40	32	5	4,2
80/20	9,3	-40	41	1,3	2,1
65/35	13,5	-38	43	1	5,0
58/42	15,7	-	82	-	4,4
50/50	17,8	-	102	-	5,6

Thermomechanical curves of OIS for the full range of NCO-groups content in the organic component are shown in Fig. 2. In accordance to the figure and data from the table two structural transitions (T_{g1} and T_{g2}), which correspond to two values of elastic deformation (L_{e1} and L_{e2}), in OIS with 6,45-13,5% of NCO-groups are observed.

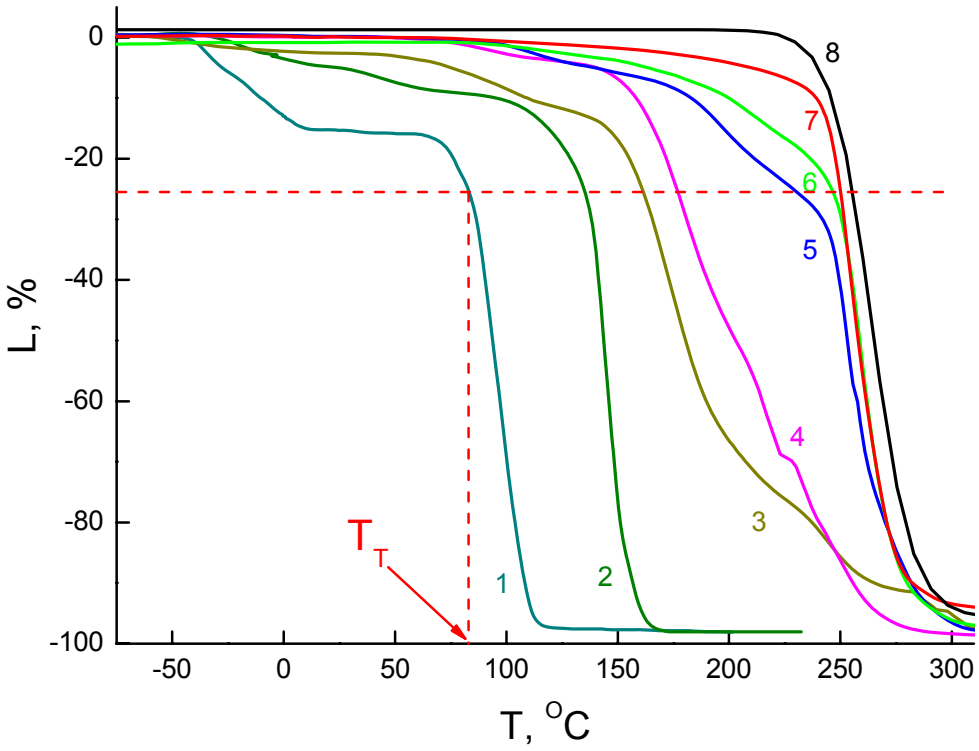

Fig. 2. Termomechanical curves of OIS with different NCO-groups content: 1 – 3,6;2 – 9,3; 3 – 13,5; 4 – 15,7; 5 – 17,8; 6 – 22,1; 7 – 26,3; 8 – 32 %.

Only one structural transition T_{g2} was found in OIS with 13,5-17,8% of NCO-groups. In OIS with the content of NCO-groups higher than 17,8% all structural transitions disappear. With increasing of NCO-groups content, the value of T_{g1} remains unchanged, while the corresponding value L_{e1} is reduced. Meanwhile, For the second glass transition temperature T_{g2} increases, while the value L_{e2} retains constant.

To evaluate the deformative properties of the synthesized compositions we have chosen the characteristic temperature T_T, which corresponds to the level of compositions strain L = 25% (dashed line in Fig. 2). Such deformation level with the temperature increasing is not related to elastic, but to the visco-plastic deformation, when the material capable of plastic flow, thereforecan T_T can be defined as the flow temperature.

Fig.3 shows the dependence of T_T on content of free NCO-groups in the organic component of OIS. As it is seen from the graph, this dependence has two regions: at once T_T value increases in the content interval of NCO-groups 3,6-17,8 (which corresponds to

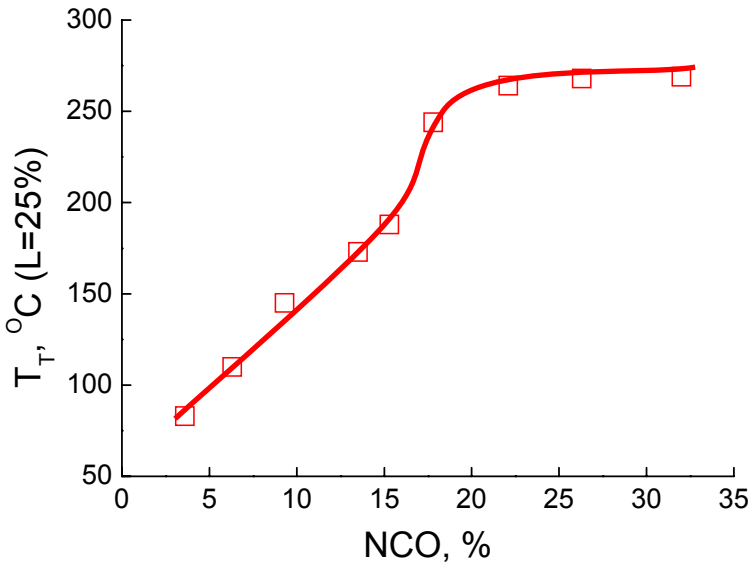

Fig. 3. The dependence of the flow temperature T_T on the NCO-groups content in OIS organic component

the changing of the MDI/PIC ratio from 100 / 0 to 50/50), and the value of T_T retains constant in the interval 17,8-32% (ratio of MDI/PIC from 50/50 to 0 / 100).

3.2. Electrical properties of OIS

Fig. 4 depicts the curves based on the results of dielectric studies. Values of permittivity ε' (blue curve) and dielectric losses *tan* δ (green curve) are rapidly diminishing

in the first area of NCO-groups concentration, and the value of ε' decreases in much narrow range of NCO-groups content (from 9.3 to 17 8%).

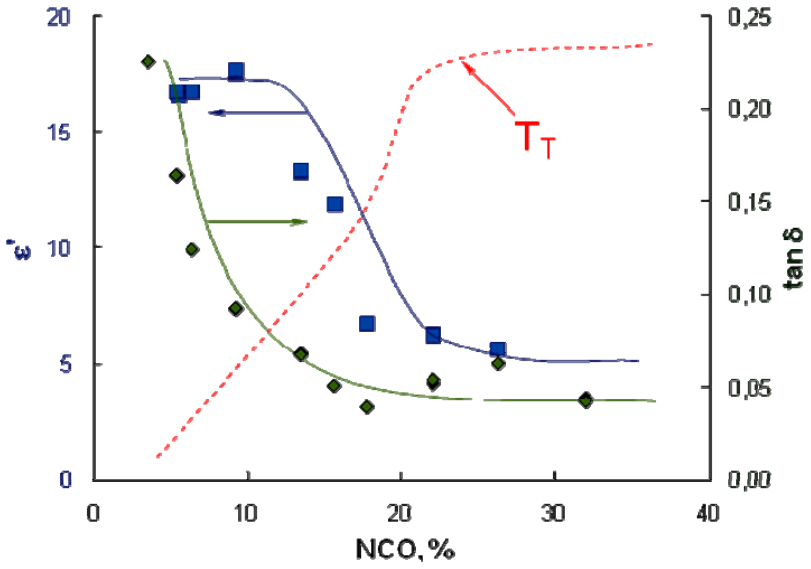

Fig. 4. Dielectric parameters of OIS

Starting from the NCO concentration equal to 17,8%, ε' and *tan* δ take constant values. For the comparison the dependence of the flow temperature T_T on NCO-groups content is given in the same picture (red curve). Apparently, a good correlation between concentration dependences of dielectric and thermomechanical parameters can be found.

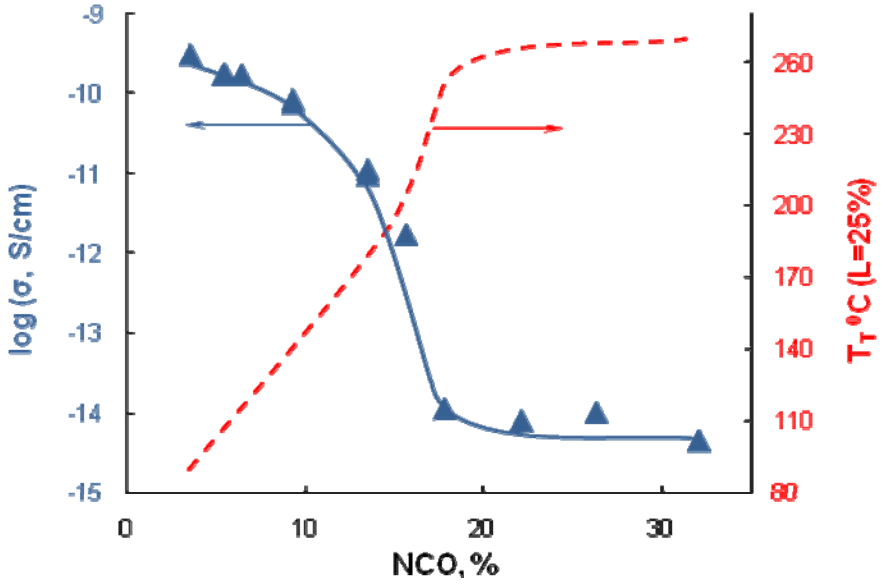

Fig. 5. The correlation between concentration dependences of conductivity σ and flow temperature T_T

Fig.5 shows the concentration dependence of DC conductivity σ. Similar to dielectric characteristics, the value of σ rapidly falls in the low content interval of NCO-groups, further it becomes constant. Easy to see that the dependence of σ (curve 1) is symmetrical relative to the dependence of T_T (curve 2) on the concentration of NCO-groups, which indicates the same nature of OIS structure impact on thermomechanical properties and charge transfer processes.

4. Discussion of results

Results of thermomechanical analysis show two glass transition temperatures T_{g1} and T_{g2} in OIS obtained. Their presence indicates the existence of two structural formations in OIS volume, which may be the result of two types of hybrid networks creation during OIS synthesis. It can be assumed that a more flexible hybrid network with a low glass transition temperature T_{g1} was occured in the reaction of macrodiisocyanate with sodium silicate, meanwhile creating polyurethane urea and urethane similar connections between organic and inorganic components of the system [13]. Such network is characterized by more long interstitial-site distance and high segmental mobility due to the relatively high molecular weight of MDI. The presence of a high glass transition temperature T_{g2} testifies to the formation of more rigid hybrid network, which may be the result of reaction between polyisocyanate and sodium silicate. This network has much shorter interstitial-site distances and limited mobility of segments. These results allowed to propose the structural model of OIS, which includes two types of hybrid networks (Fig. 6). The similar model of hybrid organic-inorganic systems was described earlier in [14].

In [7] it was established that the inorganic phase exists in the volume of OIS with the similar chemical structure as a nanoscale inclusions with dimensions about 7 nm. According to the structural model the elastic and rigid hybrid networks have been formed by the combination of the mineral phase with an organic phase, coexist in OIS volume, and the rigid network is allocated like domains in a matrix of elastic network. Such structure is characteristic for OIS with low content of NCO-groups, when the elastic network is prevailing in OIS volume. For the ratio MDI/PIC = 100 / 0 only a flexible hybrid network MDI-SS exists in OIS structure. With the further increasing of NCO-groups content the second, more rigid hybrid network appeared in reactions between PIC and SS. In the

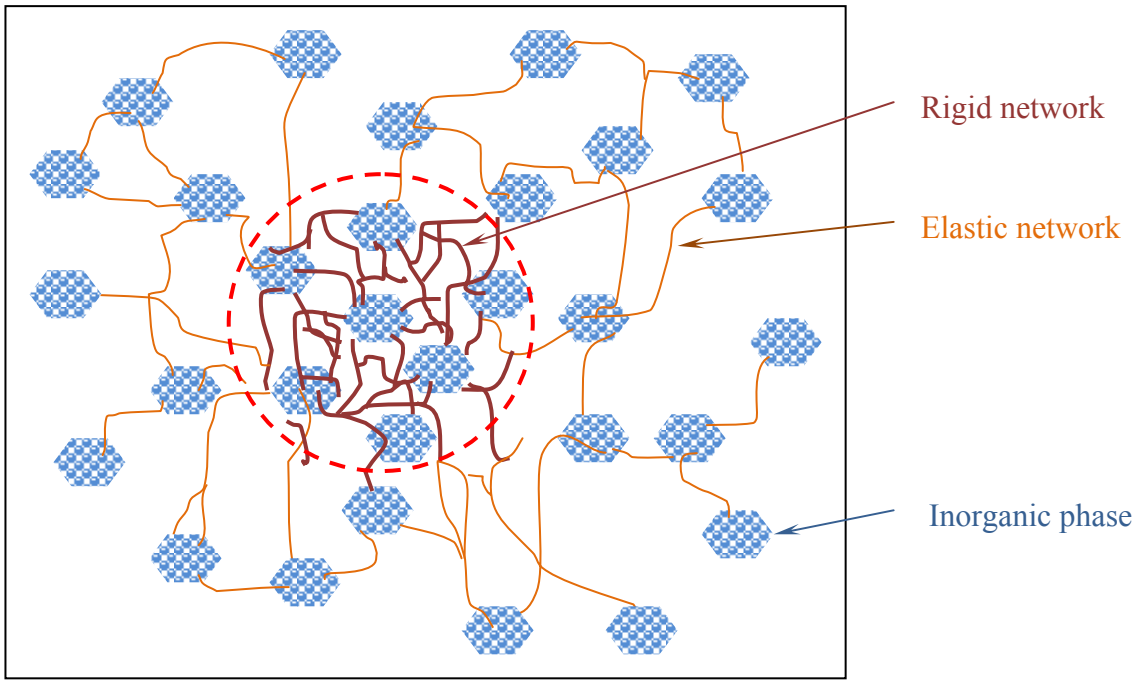

Fig. 6. OIS structural model. Hybrid rigid network inclusions in the elastic network matrix are marked by the dashed line.

content interval of NCO-groups 3,6-17,8%, which corresponds to the organic component's products ratio MDI/PIC from 100/0 to 50/50, the rigid network PIC/SS exists like domains while the flexible network MDI/SS creates a continuous structure in OIS volume. The table shows the deacresing of elastic deformation value L_{e1} while the glass transition temperature T_{g1} remains constant with the increasing of NCO-groups content. The inalterability of T_{g1} value indicates that parameters and properties of the elastic network do not change, the changes occur in the overall OIS structure by reducing the elastic network contribution and increasing contribution of rigid network in the amount of elastic deformation L_{e1}.

Unlike to T_{g1}, the value of T_{g2} grows up with the increasing of NCO-groups content, what indicates the formation of more branched rigid network. The inalterability of L_{e2} can be deduced that the elastic network is already in the plastic flow state at high temperature T_{g2} and does not give any contribution to the elastic deformation of OIS, which is determined by L_{e2} only. With exceeding of NCO-groups content 17,8% (ratio MDI/PIC equal to 50/50), the structural transition associated with temperature T_{g2} does not

appear, thus, such systems have glass transition temperature higher than flow and thermodestruction temperatures. In the composition containing NCO-groups 17,8-32% the rigid network becomes prevailing and thermomechanical characteristics of OIS hardly depend on the concentration of NCO-groups (Fig.2).

These results are confirmed by the dependence of flow temperature T_T on content of free NCO-groups (Fig.3). In the case, when the elastic network is dominant, the value of T_T is rapidly growing up, then going to OIS with the prevailing rigid network such dependence disappears. For the first area of the curve the polymer matrix consists of two types of networks - MDI-SS+PIC-SS, which determines OIS properties. In the second area of the curve the elastic network does not play any significant role, so the polymer matrix properties are defined by the hybrid rigid network PIC/SS.

This general tendency is also inherent for the dielectric and electrical characteristics of OIS. Likely, that the charge transfer process depends on the structures of both hybrid networks. The structure of elastic hybrid network MDI/SS (3,6-17,8% NCO-groups) is characterized by high permittivity ε', dielectric losses *tan* δ and conductivity σ, while for the rigid network PIC/SS (17,8-32% NCO-groups) these features is much lower and almost independent of ratio MDI/PIC. Such difference of hybrid networks can be explained by the fact that elastic network MDI/SS is hydrophilic [7, 8], and cause of high values of σ, ε' and *tan* δ can be the presence of water molecules in the network. At the same time, rigid network PIC/SS is hydrophobic with very low absorption properties.

5. Conclusions

In the reaction of the organic oligomer (macrodiisocyanate + polyisocyanate), which has free NCO-groups and the inorganic component (sodium silicate), existing in oligomeric form, organic-inorganic systems were obtained.

The structure of OIS is a system of two interpenetrating hybrid networks that are different in composition and properties. Flexible hybrid network exists as a result of reaction between MDI (which is characterized by relatively high molecular weght) and SS, and hybrid rigid network formed in reactions of PIC and SS. Depending on the composition of OIS one network is prevailing and forms a continuous structure with inclusions of the second network.

Electrical and dielectric characteristics (σ, ε' and $tan\ \delta$) are significantly different for these two types of hybrid networks: network MDI/SS is characterized by high values of σ, ε' and $tan\ \delta$, while much smaller value of these parameters is inherent for the network PIC/SS.

Thermomechanical, electrical and dielectric properties of OIS can widely regulated by changing the composition of organic phase MDI/PIC.

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Electrical and dielectric behavior of OIS.
Relaxation phenomena of OIS.
Extended structural model

4.1. Introduction

4.2. Dielectric and electrical properties of hybrid organic-inorganic polymer systems

4.3. Relaxation processes in hybrid organic-inorganic polymer systems polymerized *in situ*

Chapter 4

Electrical and dielectric behavior of OIS. Relaxation phenomena of OIS. Extended structural model

4.1. Introduction

Electrical and dielectric properties of synthesized hybrid organic-inorganic systems were studied using AC and DC methods. The results of these investigations were compared with the results of previously fulfilled thermomechanical investigations. It was shown that the elastic hybrid network is characterized by relatively high conductivity ($\sigma_{DC}\approx10^{-9}$ S/cm) and permittivity ($\varepsilon'\approx16$), whereas the rigid hybrid network has low level of conductivity ($\sigma_{DC}\approx10^{-15}$ S/cm) and permittivity ($\varepsilon'\approx5$). It was explained by the different levels of mobility of charge carriers in various hybrid structures. In weekly cross-linked structure of elastic hybrid network the charge transport is relatively free, while it is very limited in highly cross-linked structure of rigid hybrid network. Similarly to thermomechanical properties, electrical and dielectric properties are defined by the predominant hybrid network.

The relaxation spectra of hybrid organic-inorganic systems were studied using DSC, DMTA and DRS methods. Various relaxation processes that correspond to different structural formations (interpenetrating networks, interphases etc) were found. On the basis of the results obtained the extended spatial structural model of hybrid organic-inorganic systems is proposed.

4.2. Dielectric and electrical properties of hybrid organic-inorganic polymer systems

The extended description and the results of investigations of dielectric and electrical properties of hybrid organic-inorganic systems are represented in the attached publication (Page 88).

4.3. Relaxation processes in hybrid organic-inorganic polymer systems polymerized *in situ*

The extended description and the results of investigations of relaxation phenomena of hybrid organic-inorganic systems are represented in the attached publication (Page 100).

Dielectric and thermal-mechanical properties of hybrid organic-inorganic polymer systems based on isocyanate-containing oligomers[4]

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Abstract

Hybrid organic-inorganic polymer systems (OIS) were obtained in reactions of the organic oligomer (macrodiisocyanate + poly(isocyanate) (MDI+PIC)) which have free isocyanate groups with inorganic oligomer - sodium silicate (SS). The structure of OIS was formed as two interpenetrated networks: an elastic network as a result of reactions MDI-SS and a rigid network PIC-SS resulting respectively from the reaction of MDI with SS and PIC with SS. Depending on MDI/PIC ratio, one of the networks features is prevailing as attested by dielectric, electrical and thermal-mechanical experiments. The elastic network MDI-SS possesses high values of dielectric parameters ε', tan δ and conductivity σ whereas for the rigid network PIC-SS the values of these characteristics are much lower and are typical for usual thermosets.

Keywords: *organic-inorganic composites, hybrid systems, interpenetrating networks, oligomer, isocyanate groups, dielectric properties, conductivity, thermal-mechanical properties.*

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1. Introduction

Over the last years the study of hybrid organic-inorganic systems (OIS) has attracted an attention of researchers because of the possibility of obtaining of a variety of properties owing to the specific chemical structure of OIS that includes chemically bonded organic and inorganic blocks [1, 2]. In particular, due to the presence of ionic conductivity, the use of OIS as solid electrolytes and membranes for fuel cells is a promising perspective [3, 4]. Some types of OIS demonstrate high chemical and radiation resistance [5] and thermal stability [6, 7]. Depending on chemical composition, OIS allow to obtain a wide range of electrical, dielectric [8, 9] and sorption characteristics [8, 10] .

At present time the most suitable route of obtaining of OIS is the sol-gel technology [1-3, 11] which is the most effective for the synthesis of tailored organic/inorganic systems. However this multi-step process involves rather complicated reactions. The original method of OIS synthesis by polymerisation of mixture of the liquid organic and inorganic oligomers, which have the reactive groups, has been proposed in [10-12]. By changing the chemical composition of the organic and inorganic oligomers and their ratio the properties of final product, OIS, can be varied in wide range.

In present work the hybrid organic-inorganic polymer systems that were obtained as a result of reaction of the organic oligomer (the mixture of macrodiisocyanate + poly(isocyanate), which contain free isocyanate groups) with sodium silicate have been studied. Using of a mixture of macrodiisocyanate and poly(isocyanate) enables to vary the content of NCO-groups in the organic component and therefore to change the OISs structure. The measurements of dielectric, electrical and thermal-mechanical characteristics of OIS in wide temperature range depending on composition of OIS were fulfilled.

2. Experimental

2.1. Materials and synthesis.

Organic component of OIS consists of two isocyanate-containing products:

- macrodiisocyanate (MDI) with Mw = 4500 which contains 3,6 % of free NCO-groups;

- poly(isocyanate) (PIC) that have a composition 50/50 of diphenylmethandiisocyanate(Mw=250)/iso-cyanate isomers and which contains 32 % of free NCO-groups.

Urethane oligomer MDI was synthesized on the base of 2,4-toluene diisocyanate and oligooxypropylene-glycol with Mw = 2100. PIC of type D was used.

Weight ratio MDI/PIC was varied in the range from 0/100 to 100/0.

Inorganic component was sodium silicate (SS) existing in the form of oligomer in the water solution with general formula

$$aNa_2O \cdot bSiO_2 \cdot cH_2O$$

where b/a is silicate module. Industrial sodium silicate with characteristics defined by national standard GOST 13078-81 was used. The value of b/a is equal to 2,8, and density – 1,45 g/cm^3. Detailed characteristics of the products was given in [10].

Synthesis of OIS was fulfilled in reactive mixture of organic and inorganic oligomers, the reactions of synthesis were described in [11, 12]. The reactive mixture placed in the Teflon mould where the reactive mixture was cured during 25 h at room temperature (T=22±1 ^{0}C). The ratio organic/inorganic components (MDI+PIC)/SS=70/30 for all cases.

2.2. Equipment and measurements

Dielectric characteristics (dielectric constant ε′ and dielectric loss tangent tan δ) were measured by bridge P5083 Rostok-prylad (Kyiv, Ukraine) with frequency 1 kHz at room temperature.

Electrical conductivity on direct current (DC) was measured by teraohmmeter E6-13A Radiotechnika (Riga, Latvia) with applied voltage equal to 100 V.

Thermal-mechanical measurements were carried out with the hand-made equipment for TMA (thermal-mechanical analysis) in the indenting mode with the indentor of 3 mm in diameter, having the flat end, under constant load of 10 kg/cm^2. Temperature sweep was done from –120 to +350 ^{0}C with a scan rate of 3 ^{0}C/min.

Dielectric and electrical measurements were carried out with disc shape samples with 30 mm in diameter and thickness of 1,5 mm. The samples with diameter of 12 mm and thickness of 1 mm were used for thermal-mechanical measurements.

3. Results

3.1. Dielectric/electrical properties of OIS

Fig. 1 shows the values of dielectric parameters of the OIS depending on MDI/PIC ratio i. e. on content of NCO-groups in the organic part of composite. The values of ε' and $tan\ \delta$ of the composites demonstrate different behaviors for low and high contents of NCO-groups. In the range of NCO-groups content equal to 3,6-17,8 % the values of ε' and $tan\ \delta$ sharply decrease, and within the interval of 17,8-32 % they become constant. In the first region, ε' and $tan\ \delta$ have rather high values, for example $\varepsilon' \fallingdotseq 18$ and $tan\ \delta = 0{,}23$ in the composite with NCO = 3,6 %.

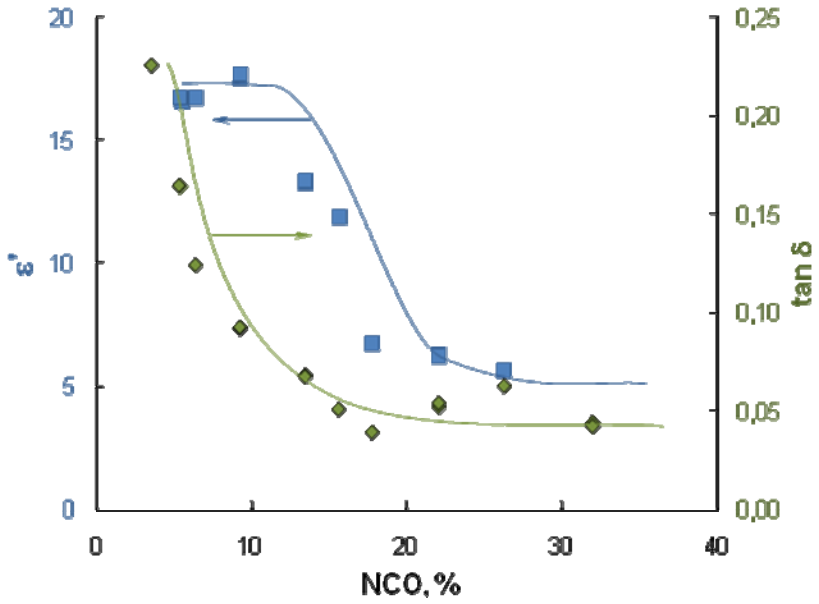

Fig. 1. Dependence of dielectric parameters ε' and $tan\ \delta$ on content of free NCO-groups in the organic part of OIS.

Concentration dependence of conductivity σ is shown on Fig. 2. Similar to dielectric parameters, the value of σ drastically drops in the range of low content of NCO-groups 3,6-17,8 %, for the further rise of NCO-groups the value of conductivity becomes constant. The change of conductivity is about 5 orders of magnitude that testifies to the sufficient changes in the OIS structure.

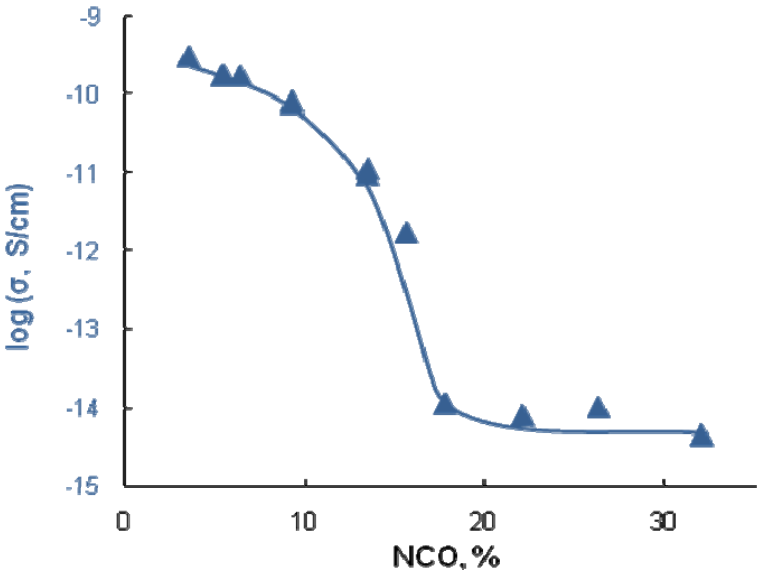

Fig. 2. Dependence of conductivity σ on content of free NCO-groups in the organic part of OIS.

3.2. Thermal-mechanical properties of OIS

In Fig. 3-a the general thermal-mechanical curve (dependence of relative deformation of the sample *L* on temperature T) of OIS with ratio MDI/PIC=90/10 (that corresponds to content of the NCO-group equal to 6,5 %) is shown.

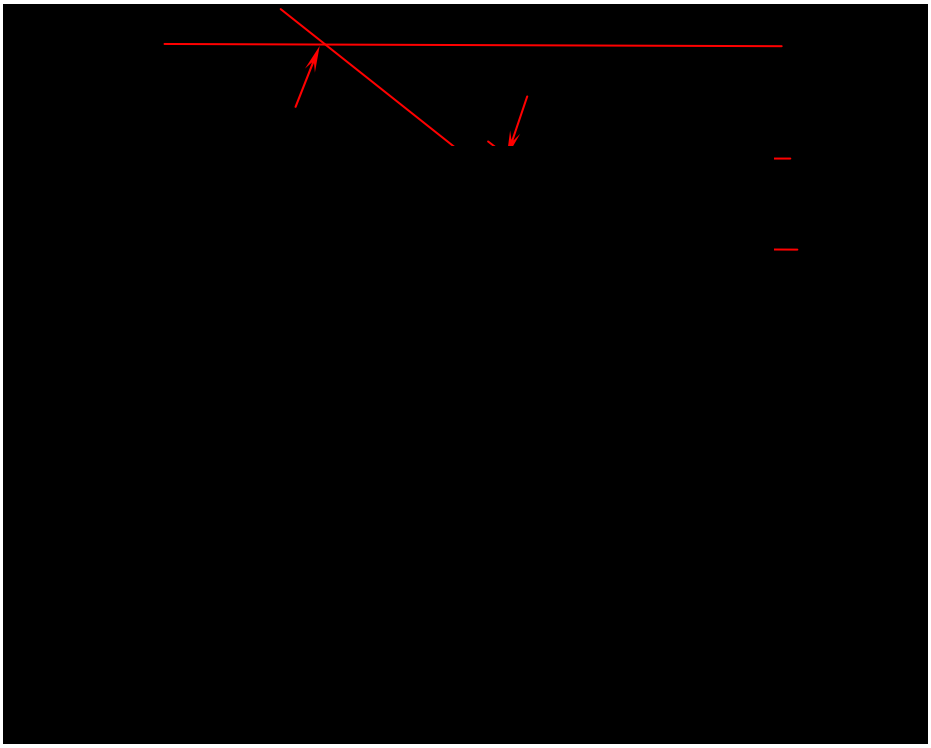

Fig. 3. a - Thermal-mechanical curve of the sample with NCO-group content equal to 6,5 %; b - enlarged part of curve for lower deformation (up to 25 %).

Relative deformation L, % was defined by relationship

$$L = \frac{\Delta L}{L_0} \cdot 100 \qquad (1)$$

where ΔL is deformation, μm; L_0 is initial thickness of the sample, μm.

As one can seen, two regions of the elastic deformation can be observed on the curve, which are more pronounced in Fig. 3-b in the enlarged scale. These two regions appear as a result of transitions from the glass to the elastic state and can be characterized by following parameters: the glass-transition temperatures T_{g1}, T_{g2} and the values of elastic deformation L_{e1}, L_{e2} (see Fig 3-b). The values of T_g and L_e are listed in the Table 1.

Table 1. Parameters of the glass-transitions for OIS with different content of NCO-groups in organic part of composite.

MDI/PIC	NCO, %	T_{g1}, ^{0}C	T_{g2}, ^{0}C	L_{e1}, %	L_{e2}, %
100/0	3,6	-40	-	15,0	-
90/10	6,5	-40	32	5,1	4,2
80/20	9,3	-40	41	1,3	2,1
65/35	13,5	-38	43	1,0	5,0
58/42	15,5	-	82	-	4,4
50/50	17,8	-	102	-	5,6

These data evidence that OIS consists in two interconnected structures differing by the intensity of their molecular motions.

The TMA curves for OIS in all range of existence of the NCO-groups are shown in Fig. 4. The evolution of curves demonstrates that first glass-transition T_{g1} at –40 ^{0}C decreases rather quickly. Second glass-transition T_{g2} is more stable and exists up to content of NCO-groups equal to 17,8 %. At higher concentration of NCO-groups the glass-transition T_{g2} disappears as well.

The values of T_{g1} are constant whereas the values of L_{e1} decrease when the content of NCO-groups rises. On the contrary, for the second structural transition the values of T_{g2} grow whereas L_{e2} maintain their values.

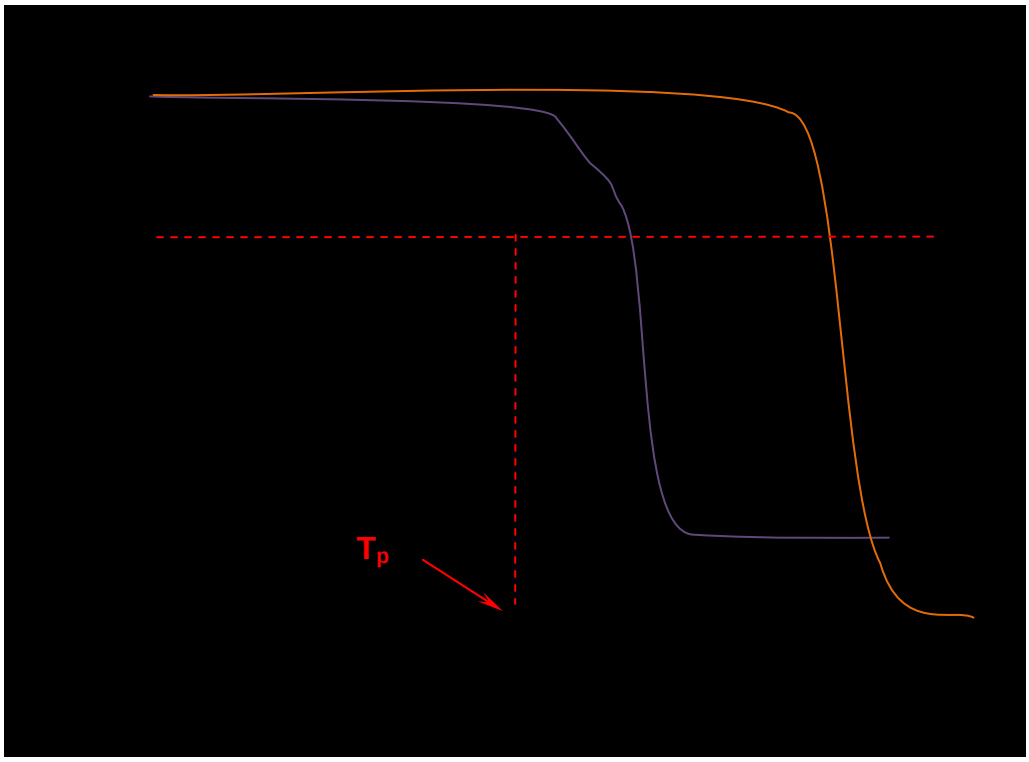

Fig. 4. Thermal-mechanical curves for OIS with content of NCO-groups: 1 – 3,6, 2 – 9,3, 3 – 15,7, 4 – 17,8, 5 – 26,3, 6 – 32 %. T_p is temperature of plasticity on the level of deformation L=25 %.

The TMA curve in Fig. 3-a demonstrates that the region of plasticity begins at higher than 120 ^{0}C for this composition of OIS and the sample is completely deformed at 180 ^{0}C ($L \rightarrow 100$ %). The deformation in this temperature region is caused by plastic flow of material. In order to evaluate the temperature position of the transition from the elastic deformation to the plastic deformation, the temperature of plasticity T_p that corresponds to the level of plastic deformation L=25 % has been chosen (dotted line in Fig. 4). Fig. 5 shows the dependence of T_p on the NCO-groups content in OIS. As it can be seen, in the interval of concentration of the NCO-groups equal to 3,6-17,8 % the value of T_p rapidly grows while in the region of 17,8-32 % T_p is constant. For comparison, the curves for permittivity ε' and conductivity σ dependencies are given in this figure as well (dotted lines), this will be discussed later.

4. Discussion

The presence of two glass transition temperatures T_{g1} and T_{g2} in OIS is an evidence of two types of the structure formation in the volume of OIS that can be as a result of the

creation of two types of the hybrid networks during synthesis. One can assume that more elastic hybrid network with low glass transition temperature T_{g1} appears as the result of reaction of MDI having relatively high molecular weight (Mw) [11] with sodium silicate.

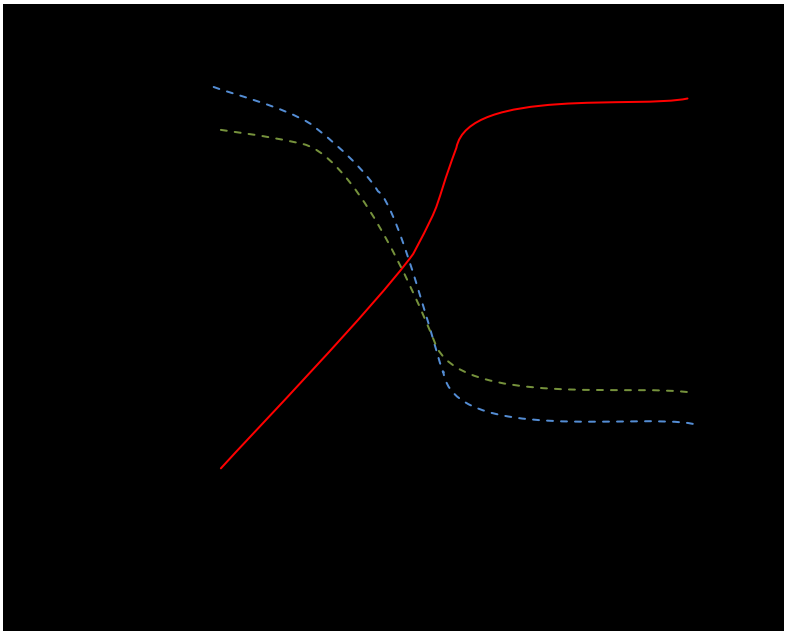

Fig. 5. 1 - dependence of T_p on concentration of NCO-groups, 2, 3 – dependencies for permittivity ε' and conductivity σ respectively.

Such a network is characterized by longer distance between cross-linking points and higher mobility of segments owing to higher Mw. Other rigid hybrid network with higher glass transition temperature T_{g2} can be created as the result of reactions of PIC with sodium silicate. It has shorter chains between cross-linking points and consequently a restricted segmental mobility. This approach allowed us to propose the structural model of OIS that includes two types of the hybrid networks (Fig. 6). Similar model of hybrid organic-inorganic system with one type of the hybrid network was described before [13].

Authors [10] have revealed (by X-ray study) that the inorganic phase exists in the volume of OIS in a form of nanosize inclusions with dimension ~ 7 nm. Consequently, the structural model shows the coexistence of elastic and rigid hybrid networks that were created by combination of the organic network with inorganic nanoinclusions. The distribution of rigid network within elastic network in a form of domains is inherent for composites with low concentration of NCO-group, when elastic network prevails in the volume of OIS.

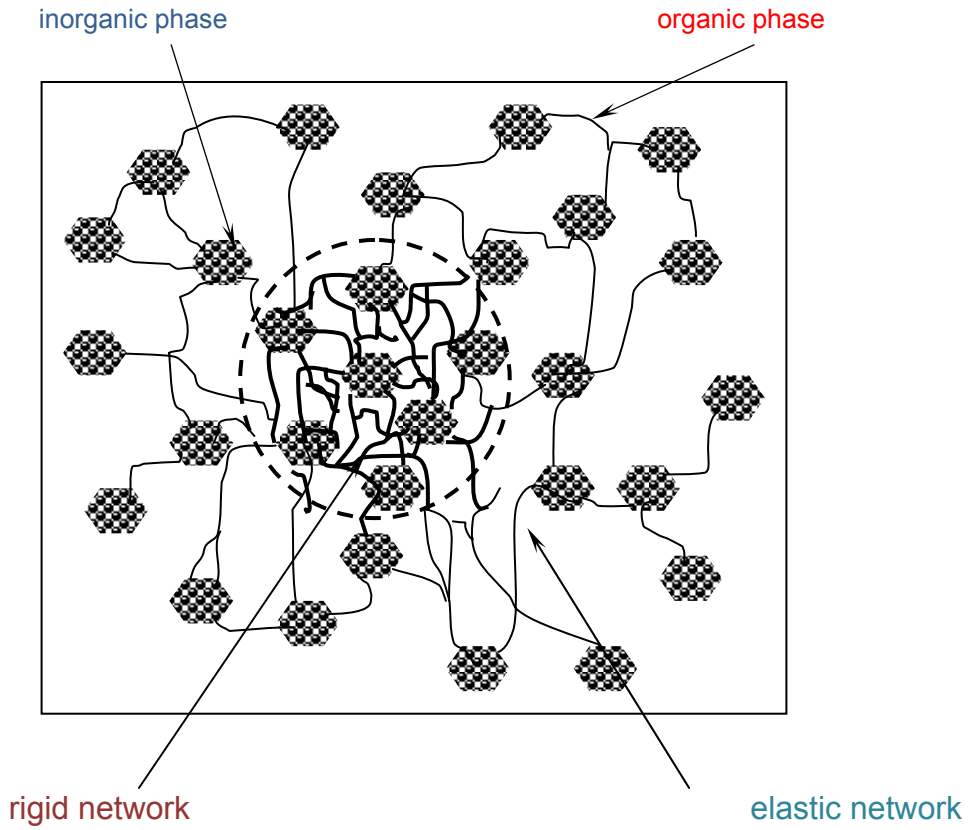

Fig. 6. Structure model of OIS. Dotted circle marks the inclusion of rigid network in the matrix of elastic network

Structural model depicts this case. Such a type of structure is resulted by evolution of the hybrid network: first, for MDI/PIC composites with ratio of 100/0 the only elastic network MDI-SS exists. Later on, increasing of PIC content (and consequently NCO-groups) leads to the appearance of second rigid hybrid network in the reactions of PIC-SS. This rigid network creates the domains inside elastic network for the range of NCO-groups content of 3,6-17,8 % (that corresponds to ratio MDI/PIC from 100/0 to 50/50).

It follows from the data of Table 1 that the values of L_{el} decrease whereas the values of T_{g1} are constant with the increasing of concentration of the NCO-groups. The constant values of T_{g1} are evidence of the maintenance of the structure and characteristics of the elastic network. The changes take place in the common structure of OIS owing to the decrease of contribution of the elastic network in the value of elastic deformation of the system L_{el}.

In contrast to T_{g1} the values of T_{g2} increase with rise of the NCO-groups that indicates creation of more crosslinked rigid network. In this case, at high temperatures

around T_{g2} the elastic network is in the regime of plastic flow and gives the negligible contribution in the elastic deformation of OIS which is defined only by L_{e2}.

The further increase of NCO-groups in OIS leads to the change of the OIS structure: rigid network PIC-SS becomes prevailing with domains of elastic network MDI-SS. In this case, however, perhaps these two types of networks can be interpenetrating . The rigid network grows faster than elastic one because of low Mw of PIC, consequently the elastic network grows slower inside of the formed rigid network creating interpenetrating structure.

It is interesting to note that in the region of 17,8-32 % of the NCO-groups the transition corresponding to T_{g2} is absent owing to the fact that T_{g2} exceeds the temperature of plasticity and thermal degradation. Although the rigid network becomes more crosslinked with the increasing of concentration of the NCO-groups, the TMA curves maintain their shape and characteristics (Figs. 4, 5). It means that plastic flow (characterized by T_p) at the content of NCO-groups higher than 17,8 % is defined not only by the structure of network but also by the thermal decomposition of hydrogen and chemical bonds of the OIS. If latter effect is prevailing then T_p does not depend on the concentration of NCO-groups. One can see this effect at T_p≈260-270 ^{0}C (Fig. 5).

The change of dielectric properties and conductivity (Figs. 1, 2) is in agreement with structural model. Obviously the charge transport depends on the structure both of networks. In the region of NCO-groups 3,6-17,8 % the dielectric parameters ε', $tan\ \delta$ and conductivity σ have high values and decrease with rise of the NCO-groups concentration. When rigid network is prevailing (range 17,8-32 % of NCO-groups) then electrical characteristics becomes constant. This strong correlation is demonstrated in Fig. 5, where the curves for T_p and for ε' and σ are almost symmetrical.

The decrease of contribution of the elastic network leads to the decrease of values of the electrical parameters. Probably it can be caused by hydrophilic properties of hybrid networks. Assuming the presence of proton conductivity in OIS, the high values of ε', $tan\ \delta$ and σ possibly derive from the presence of water in elastic network. In refs. [8, 10] high hydrophilic properties of the OIS with elastic network were shown. In some cases the water molecules which diffused into OIS create multilayered structure around nanoparticles of sodium silicate while the elastic matrix is expanded allowing to sorb big

volume of water, up to several hundreds percents [8, 10]. Correlation between water sorption and conductivity was revealed in [8]. The dielectric characteristics strongly depend on the change of type of the elastic network as well [9].

On the contrary, rigid network PIC-SS is hydrophobic and possesses very low values of water sorption and high chemical resistance [5]. In this case the proton conductivity caused by water is negligible. The values of dielectric characteristics and conductivity in the second region of the NCO-group concentration are typical for usual thermoset polymers, for example for epoxy resin.

5. Conclusions

Hybrid organic-inorganic polymer system (OIS) was obtained by the reaction of the organic oligomer that was a mixture of two isocyanate-containing products: macrodiisocyanate+polyisocyanate (MDI+PIC)) with inorganic component – water solution of sodium silicate (SS) that exist in a form of oligomer. MDI had 3,6 % of free isocyanate groups and PIC had 32 % of NCO-groups. Changing their ratio the properties of OIS were varied.

The structure of OIS exists in a form of two interpenetrating networks: the elastic network as a result of reactions of MDI with higher molecular weight with SS and rigid network that is created in the reactions of low-molecular PIC with SS. Depending on MDI/PIC ratio one of the networks is prevailing and creates continuous structure with domains of second network.

Dielectric, electrical and thermal-mechanical properties are strongly different for two types of networks. The elastic network MDI-SS possesses high values of dielectric parameters ε', $tan\ \delta$ and conductivity σ whereas for the rigid network PIC-SS the values of these characteristics are much lower and are typical for usual thermosets. By changing of MDI/PIC ratio in the organic phase properties of OIS can be varied in wide range.

6. Acknowlegments

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Relaxation processes in hybrid organic-inorganic polymer systems polymerized *in situ*[5]

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Abstract

The relaxation processes of hybrid organic-inorganic polymer systems (OIS) synthesized by joint polycondensation were studied. The organic component was the mixture of two products: high-molecular macrodiisocyanate with low reactivity and low-molecular isocyanate-containing modifier poly(isocyanate) (PIC) with high reactivity. Sodium silicate (SS) was used as inorganic component. The structures of OIS obtained were in the form of hybrids with covalently connected building blocks and interpenetrating networks: the weakly cross-linked network MDI/SS and highly cross-linked network PIC/SS. Depending on MDI/PIC ratio one of the networks was prevailing and created continuous structure with domains of second network.

Keywords: *organic-inorganic composites, hybrid systems, joint polycondensation, interpenetrating networks, relaxation phenomena.*

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1. Introduction

Hybrid organic-inorganic polymer systems (OIS) were considered by many researches as very interesting and perspective materials due to possibility to combine chemically bonded organic and inorganic blocks in one structure and, therefore, to synthesize compositions with their common properties, thus obtaining materials with specific characteristics [1, 2]. In the course of many works on hybrid systems the use of OIS as industrial materials (for example, as solid electrolytes and membranes for fuel cells [3, 4], due to the presence of ionic conductivity, as coatings because of their high chemical, radiation resistance and thermal stability [5-7] etc.) is a promising perspective.

The investigation and understanding the structure/properties relationships is major aim of the material science [8-10]. Many essays are given to the investigation of the relaxation behavior of various materials because of ability to receive the information of these relationships.

The most usual route to the preparation of hybrid organic-inorganic systems is sol-gel process, which is the most effective for the synthesis of tailored organic-inorganic systems [1-3, 11]. However this multi-step process involves rather complicated reactions. Joint polycondensation is the new original method of OIS synthesis, which, opposite to sol-gel method, is very attractive from a technological point of view [10-12]. The major concept of this method is the polymerization of OIS in reactive mixture of the liquid organic and inorganic oligomers, which have the reactive groups. By changing of chemical composition of the organic and inorganic oligomers and their ratio the properties of final product, OIS, can be varied in wide range.

Previously in [13-17] it was reported that OIS synthesized by joint polycondensation based on various organic oligomers and sodium silicate as inorganic component are characterized by different properties depending on formed structure. In the present work the relationships between structure and properties of such OIS will be established using the information on their relaxation behavior.

2. Experimental

2.1. Materials and synthesis.

Organic component of OIS consists of two isocyanate-containing products:

- urethane oligomer – macrodiisocyanate (MDI) with Mw = 4500, which contains 2 free reactive NCO-groups. MDI was synthesized on the base of 2,4-toluene diisocyanate and oligooxypropylene-glycol with Mw = 2100.

- low-molecular isocyanate-containing modifier - poly(isocyanate) (PIC) with Mw = 450 and 3 free reactive NCO-groups. PIC was based on a composition 50/50 of diphenylmethandiisocyanate (Mw=250) / iso-cyanate isomers. PIC of type D was used.

Inorganic component was sodium silicate (SS) existing in the form of oligomer in the water solution with general formula

$$aNa_2O \cdot bSiO_2 \cdot cH_2O$$

where b/a is silicate module. Industrial sodium silicate with characteristics defined by national standard GOST 13078-81 was used. The value of b/a is equal to 2,8, and density – 1,45 g/cm^3. Detailed characteristics of the products were given in [10].

OIS were synthesized *in situ* in reactive mixture of organic and inorganic oligomers, the reactions of synthesis were described in [11, 12]. Weight ratio MDI/PIC was varied in the range from 0/100 to 100/0 that gave the opportunity to change the reactivity of organic component. The ratio organic/inorganic components (MDI+PIC)/SS=70/30 for all cases. The reactive mixture was placed in the Teflon mould where the curing passed during 24 h at room temperature (T=22±1 ^{0}C).

2.1. Equipment and measurements.

Differential scanning calorimetry investigations (DSC) were carried out using TA Instruments 2920 MDSC V2.6A in helium and air atmosphere in the range of temperature from -100 - +400 ^{o}C depending on thermostability of OIS, which was previously studied by TA Instruments TGA Q50, with cooling/heating rate was equal to 10 ^{o}C/min.

Dynamic mechanical thermal analysis (DMTA) was performed by TA Instruments DMA 2980 in single cantilever mode. The range of frequency was taken from 1 to 30 Hz,

the amplitude of oscillation was chosen 20±0,001 μm, the temperature interval was from -100 to +400±0,1 °C with the heating rate 3±0,1 °C/min. Samples were in the form of blade with the thickness h=1±0,01 mm, width d=6±0,01 mm and length l=40±0,01 mm.

Data of DMTA and DSC measurements were analyzed utilizing TA Instruments Universal Analysis 2000 ver. 3.9A.

Using dielectric relaxation spectroscopy (DRS) methods allows studying the dielectric relaxation phenomena of OIS. DRS spectra were obtained by Novocontrol Alpha High Resolution Dielectric Analyzer with Novocontrol Quatro Cryosystem equipped with two-electrode scheme. The range of frequency was 10^{-2} – 10^{7} Hz, the temperature interval was from -100 to +400±0,01 °C, the cooling/heating rate equaled to 3 °C/min. Data was analyzed using Novocontrol WinDETA ver 3.8 and Novocontrol WinFIT ver 2.8.

3. Experiment results

It is known [18, 19], that the reactivity of components (organic as well as inorganic), which enter into a reaction, is a relative value, which consists several parameters. Length of molecular chain (molecular weight Mw) and number of reactive groups are the major parameters. Viscosity (mobility of molecular chains), which can exerts some impact on the reactivity, is neglected. Therefore, for the first approximation, the reactivity of a component, in which functional groups take a part in reactions, can be calculated using equation (1):

$$R = \frac{x \cdot Mw_{react}}{Mw_{comp}} \quad (1)$$

where R – the reactivity of a component, x – number of reactive groups, Mw_{react} – molecular weight of reactive groups, Mw_{comp} – molecular weight of a component.

In such case, for multi-component system, the reactivity is determined by additive contributions of components. The equation (1) gains the view:

$$R = \sum_{i=1}^{n} m_i \cdot \frac{x_i \cdot Mw_{react}}{Mw_{i\,comp}} \quad (2)$$

where m_i is content of i component, x_i is number of reactive groups in ***i*** component, Mw_{react} is molecular weight of reactive groups, $Mw_{i\ comp}$ is molecular weight of ***i*** component.

The equation (2) is true if reactive groups of all components have an identical chemical structure.

In our case, for two-component system, in which reactive groups are NCO-groups, the equation (2) is written:

$$R = m_{MDI} \cdot \frac{x_{MDI} \cdot Mw_{NCO}}{Mw_{MDI}} + m_{PIC} \cdot \frac{x_{PIC} \cdot Mw_{NCO}}{Mw_{PIC}} \quad (3)$$

where m_{MDI} and m_{PIC} are contents of MDI and PIC, respectively, x_{MDI}=2 and x_{PIC}=3 are numbers of NCO-groups in MDI and PIC, Mw_{NCO} is molecular weight of NCO-group, Mw_{MDI} and Mw_{PIC} are molecular weights of MDI and PIC.

The compositions and reactivity of organic component of hybrid systems are shown in table 1.

Table 1. Reactivity and compositions of organic component of hybrid systems

Reactivity R	MDI, %	PIC, %
0,04	100	0
0,1	80	20
0,14	65	35
0,16	58	42
0,18	50	50
0,22	35	65
0,26	20	80
0,32	0	100

3.1. DSC results

Fig. 1 represents the DSC curves of OIS with different organic component reactivity. One can see the presence of several endothermic processes on the curves, which confirm the existence of some structural formations in OIS volume and correspond to their glass transition temperatures. The temperatures of glass transitions are introduced in the table 2. For composition with reactivity *R* of organic component equal to 0,04, which concerns the presence only of high-molecular MDI in organic part, one glass transition process nearby -50 ^{o}C can be found. This testifies to the effect that this glass transition temperature corresponds to elastic hybrid organic-inorganic network MDI/SS, which was

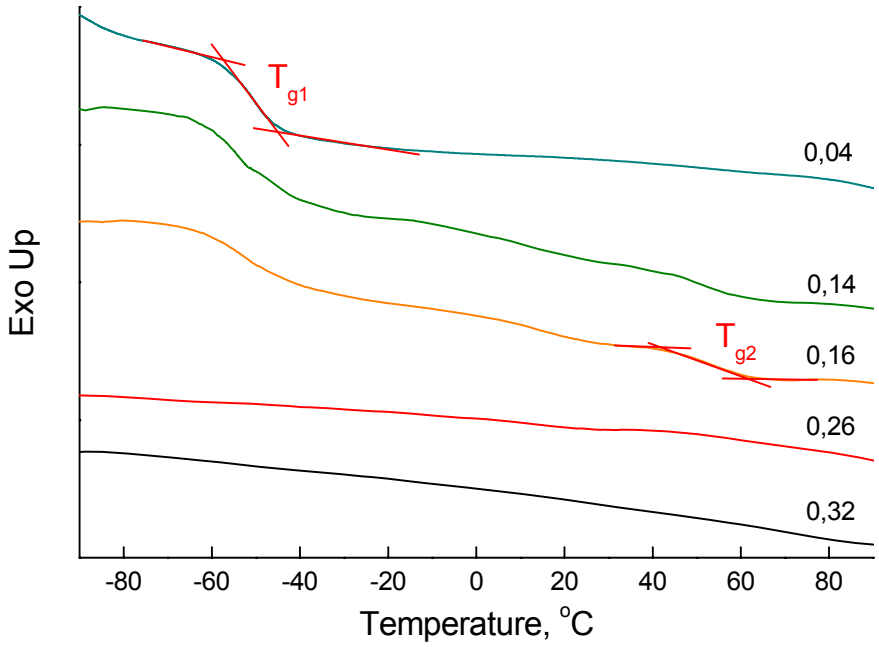

Fig. 1. DSC curves of OIS with different organic component reactivity

Table 2. DSC studies. Compositions and glass transition temperatures of OIS

	Compositions		Glass transition temperatures	
Reactivity R	MDI, %	PIC, %	T_{g1}, °C	T_{g2}, °C
0,04	100	0	-50	-
0,1	80	20	-48	39
0,14	65	35	-53	54
0,16	58	42	-58	55
0,18	50	50	-63	59
0,22	35	65	-70	67
0,26	20	80	-76	74

obtained in reactions between NCO-groups of MDI and OH-groups of SS.

With increasing the reactivity of organic component adding PIC in the reactive mixture, the second glass transition temperature appeared nearby 40 °C. Thus, it can be

referred to the more rigid hybrid organic-inorganic network PIC/SS, which is formed in reactions between NCO-groups of PIC and OH-groups of SS, accordingly. With reactivity rise the T_{g1} shifts to lower temperatures, whereas the tendency to grow up is observed for T_{g2}. T_{g1} shift is due to the presence of low molecular product, which appeared during polymerization and plays the role of plasticizer for elastic network MDI/SS. Concerning T_{g2} the plasticizing effect is weak in comparison with strong impact of growing and cross-linking of rigid hybrid network PIC/SS.

3.2. DMTA results

Results obtained using DMTA showed the presence of two-tree relaxation processes depending on the composition of OIS as it is represented in Fig. 2 and Fig. 3. The temperatures of these relaxation processes are noted in the table 3. Relaxation temperatures T_{r1} and T_{r2} as well as glass transition temperatures T_{g1} and T_{g2} correspond to hybrid networks MDI/SS and PIC/SS, respectively. Good correlation of the values and shifts of relaxation temperatures and glass transition temperatures was revealed. The third weak relaxation process T_{r0} nearby -90 °C, which corresponds to the relaxation of low-molecular product that plays the role of plasticizer for hybrid networks, was discovered.

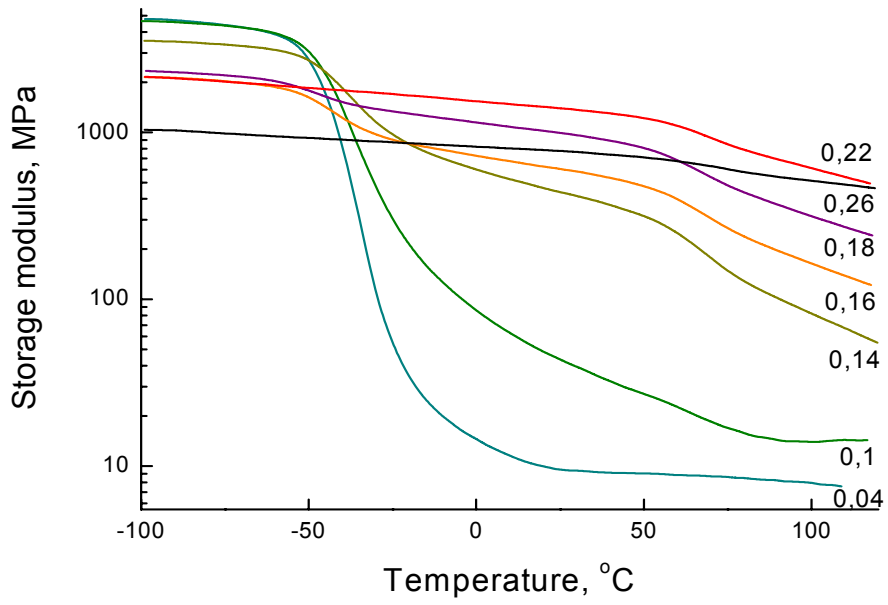

Fig. 2. Storage modulus dependencies obtained by DMTA (ω=1 Hz) on reactivity of organic component.

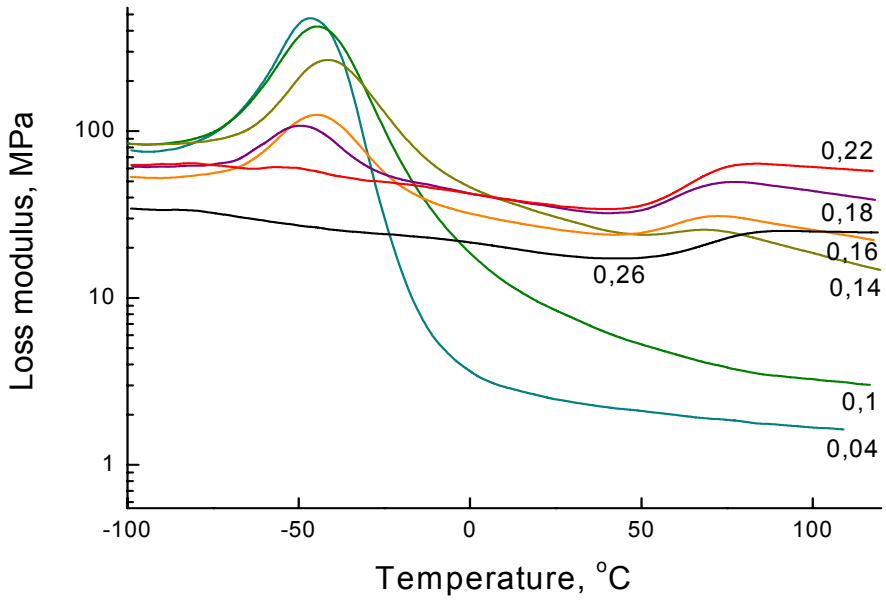

Fig. 3. Loss modulus dependencies obtained by DMTA (ω=1 Hz) on reactivity of organic component.

Table 3. DMTA studies. Compositions and relaxation temperatures of OIS

Compositions			Relaxation temperatures, ω=1 Hz		
Reactivity R	MDI, %	PIC, %	T_{r0}, °C	T_{r1}, °C	T_{r2}, °C
0,04	100	0	-94	-43	-
0,06	90	10	-92	-42	-
0,1	80	20	-89	-39	56
0,14	65	35	-79	-39	64
0,16	58	42	-76	-43	67
0,18	50	50	-73	-46	76
0,22	35	65	-71	-52	82
0,26	20	80	-69	-74	86

The rise of organic component reactivity leads to growth of a content of low-molecular product in OIS volume and, naturally, to increase its relaxation temperature and plasticizing effect.

The lessening of intensities of defrosting both hybrid networks with the rise of reactivity was observed also, as it is seen in Fig 2. and Fig. 3. This is due to the gain of content and cross-linking of rigid hybrid network PIC/SS.

3.3. DRS results

The similar tendency was revealed for dielectric and electrical characteristics (Fig. 4 and Fig. 5). The defrosting of hybrid networks leads to increasing the mobility of charge

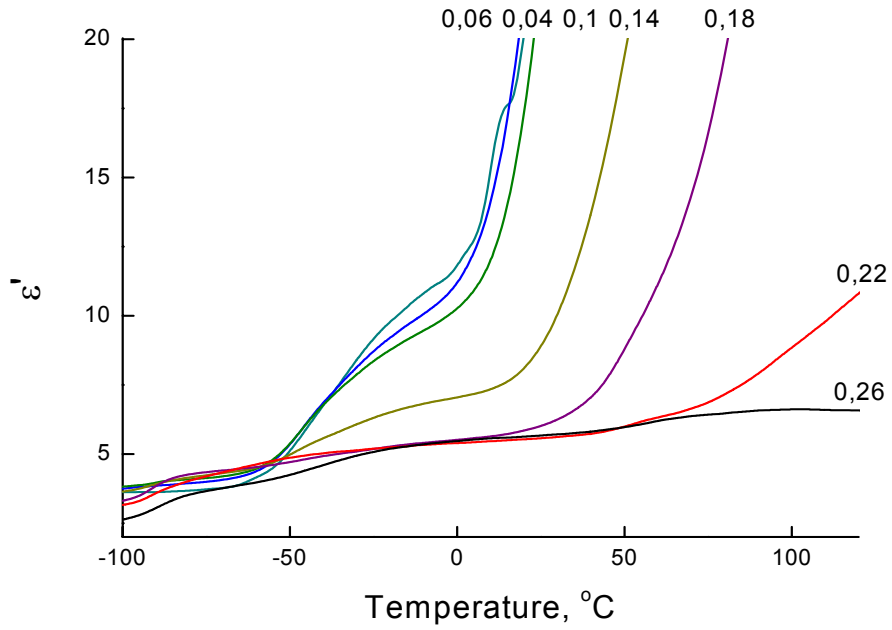

Fig. 4. Permittivity dependencies of OIS on reactivity of organic component.

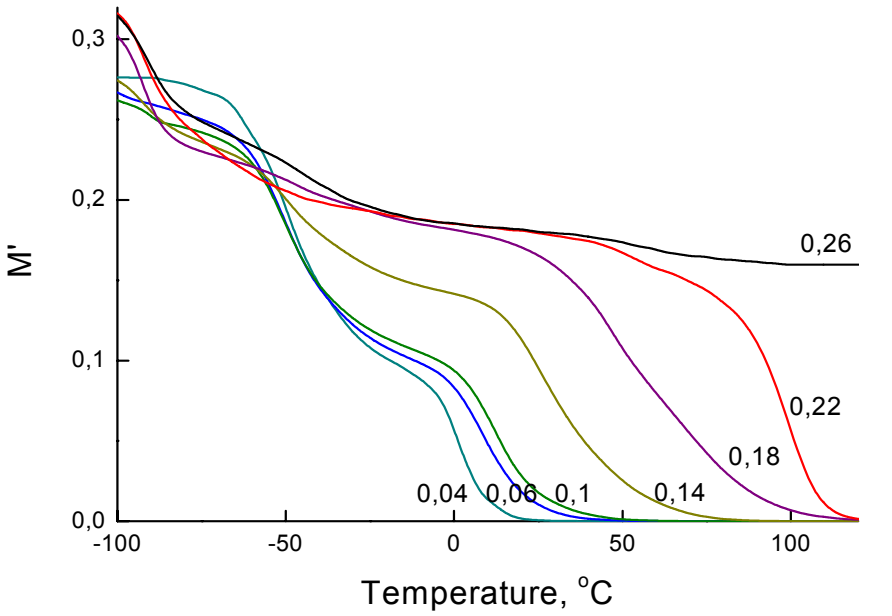

Fig. 5. Dependencies of dielectric modulus M´ of OIS on reactivity of organic component

carriers, which, in our case, were sodium ions Na^+ and water molecules H_20 (in some cases protons H^+). The rise of mobility of ions and water molecules has the stepped view in accordance to transitional defrosting of structural formations of both hybrid networks. Fig. 6 shows the dependencies of dielectric modulus M´´ on reactivity of organic component of OIS.

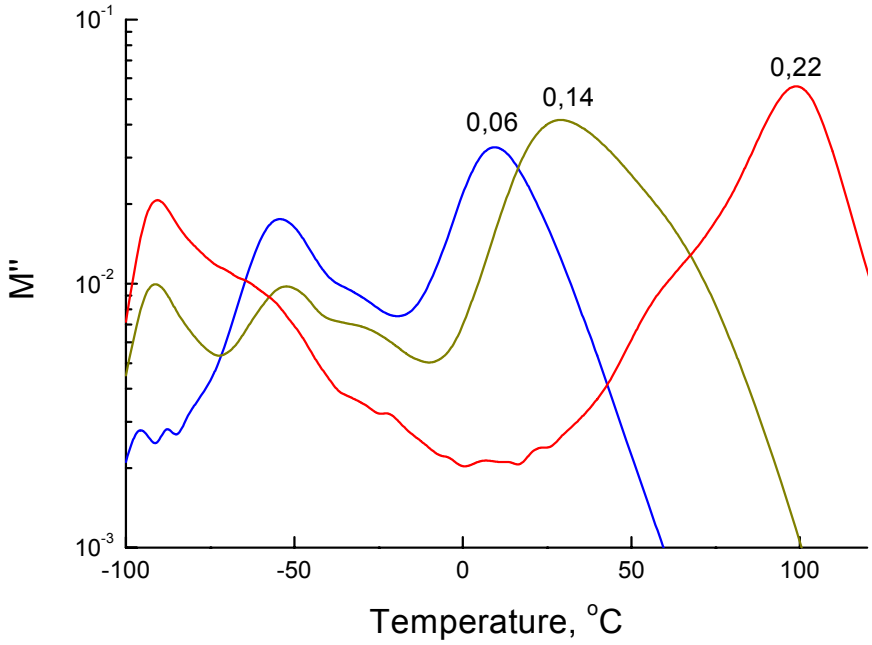

Fig. 6. Dependencies of dielectric modulus M´´ on reactivity of organic component

It is obvious, that the relaxation maximums nearby temperatures -90 °C, -50 °C and 50 °C correspond to relaxation processes of low-molecular product, hybrid network MDI/SS and hybrid network PIC/SS, respectively. In addition, two relaxation processes were found in the middle temperature range, which conform to defrosting of water molecules and interphase polarization (Maxwell-Wagner-Sillars polarization). In the sequel these relaxation will not be considered so long as they need significant additional studies, which will be presented in future applications. The relaxation temperatures of structural formations are entered in the table 4.

Table 4. DRS studies. Compositions and relaxation temperatures of OIS

Compositions			Relaxation temperatures, ω=1 Hz		
Reactivity R	MDI, %	PIC, %	T_{r0}, °C	T_{r1}, °C	T_{r2}, °C
0,04	100	0	-98	-60	-
0,06	90	10	-96	-54	-
0,1	80	20	-91	-52	41
0,14	65	35	-90	-51	59
0,18	50	50	-89	-56	70
0,22	35	65	-88	-65	98
0,26	20	80	-87	-76	108

4. Discussion

It is obvious from DSC, DMTA and DRS studies that the general properties as well as structure of hybrid systems depend on reactivity of organic component, which was regulated by variation the ratio MDI/PIC in organic component in reactive mixture during polymerization. It was shown that with the rise of reactivity of organic component by insertion and increasing the content of the isocyanate-containing modifier PIC the formed hybrid systems became more rigid and thermostable, less conductive and polarizable. The essential changes of these characteristics occurred in the middle range of reactivity of organic component, while for low and high values of reactivity they were more or less invariable. This is due to the presence of at least two hybrid organic-inorganic structures formed in the volume of OIS obtained. In hybrid systems with low reactivity of organic component the major part of organic component was macrodiisocyanate, thus the hybrid organic-inorganic network MDI/SS was the dominant structure, general properties of OIS were prevalently defined by the properties of this hybrid network. Hybrid network PIC/SS was in the form of domains in matrix of hybrid network MDI/SS. Opposite, the hybrid network PIC/SS dominated in OIS with high reactivity of organic component, general properties of OIS were prevalently defined by the properties of this network. In OIS with the middle reactivity of organic component both networks may be dominant depending on the prevailing product in organic component. The transition from domination of hybrid network MDI/SS to domination of hybrid network PIC/SS can be pointed nearby 0,18 of reactivity of organic component. Any interactions between both hybrid networks were revealed. In accordance to [20] such OIS can be referred to hybrids with covalently connected building blocks and, in some cases, interpenetrating networks. Thus, for

understanding the relationships between structure and properties of such hybrid systems it is evidently necessary to consider both hybrid networks separately.

4.1. Hybrid network MDI/SS

Hybrid organic-inorganic network MDI/SS formed in reactions of high-molecular macrodiisocyanate with two end-functional NCO-groups and sodium silicate. This network

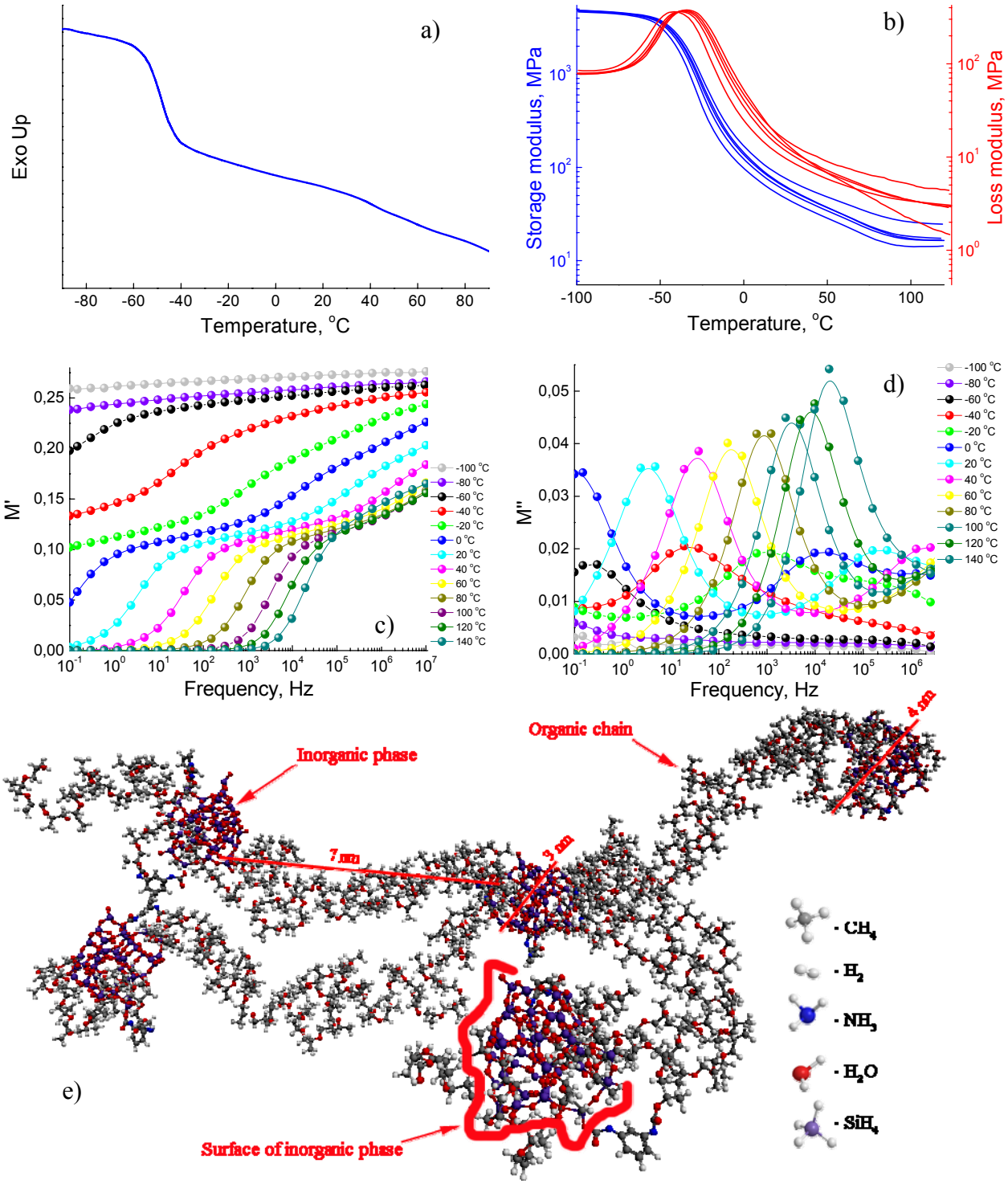

Fig. 7. DSC (a), DMTA (b), DRS (c, d) curves of OIS with R=0,06 and 3D structural model (e) of hybrid network MDI/SS

with low reactivity of organic component and glass transition temperature nearby -50 °C (Fig. 7) is characterized by high molecular mobility (Fig. 7a), elasticity (Fig. 7b), mobility of charge carriers (Fig. 7c, 7d) and, correspondingly, relatively high values of permittivity and conductivity. Long organic chains are connected to inorganic phase with two end-functional groups (Fig. 7e), thus weakly cross-linked structure is formed that has bulk adsorbed water.

4.2. Hybrid network PIC/SS

Hybrid organic-inorganic network PIC/SS obtained in reactions of low-molecular isocyanate-containing modifier poly(isocyanate) with R=0,32 and sodium silicate. This

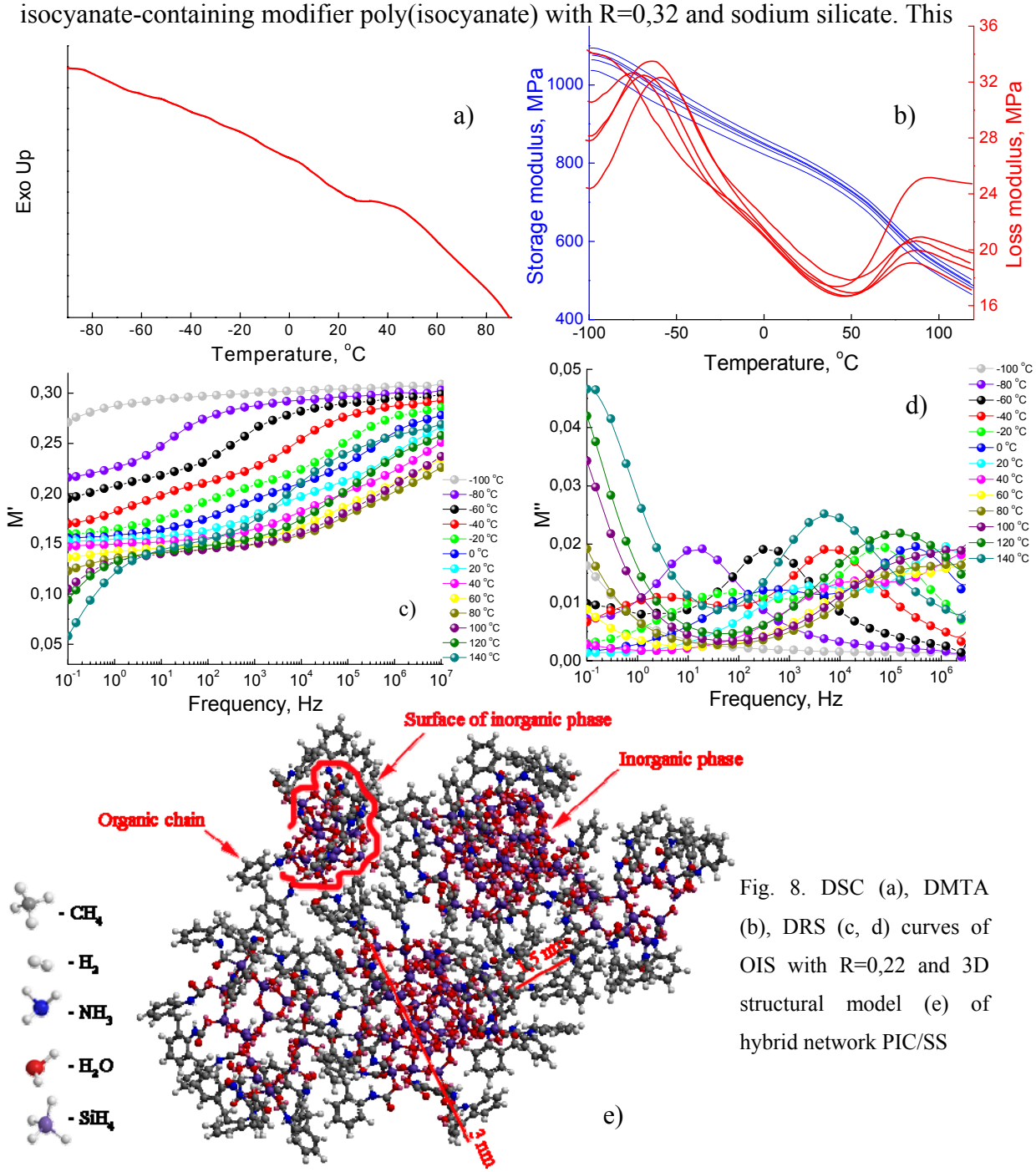

Fig. 8. DSC (a), DMTA (b), DRS (c, d) curves of OIS with R=0,22 and 3D structural model (e) of hybrid network PIC/SS

hybrid network is rigid (Fig. 8b) with glass transition temperature nearby 70 ^{o}C (Fig. 8a). The structure of this hybrid network is highly cross-linked with low molecular mobility (Fig 8e), due to short length of organic chains and high reactivity of organic component. Short organic chains with R=0,32 create continuous layer on the surface of inorganic phase. The permittivity and conductivity is low (Fig. 8c, 8d) because of impossibility of charge transport through such cross-linked structure.

5. Conclusions

Hybrid organic-inorganic polymer systems (OIS) were obtained by the reaction of the organic component that was a mixture of two products: macrodiisocyanate (MDI) and isocyanate-containing modifier poly(isocyanate) (PIC) with inorganic component – water solution of sodium silicate (SS) that exist in a form of oligomer. Changing the reactivity of organic component from R=0,04 (pure MDI) to R=0,32 (pure PIC) the structure and properties of OIS were varied.

The structure of OIS existed in a form of hybrids with covalently connected building blocks and interpenetrating networks: the weakly cross-linked network as a result of reactions of high-molecular MDI with SS and highly cross-linked network that was created in the reactions of low-molecular PIC with SS. Depending on MDI/PIC ratio one of the networks was prevailing and created continuous structure with domains of second network.

The properties of two types of hybrid networks were strongly different. The general properties of OIS were prevalently defined by the properties of dominant hybrid network.

6. Acknowlegments

This research was supported by Bourse d'Excellence Eiffel MAE and CNRS-NASU cooperation.

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Sorption and sensory activity of OIS. Perspectives of OIS utilization

5.1. Introduction
5.2. Sorption activity of hybrid organic-inorganic polymer systems
5.3. Sensory conductive organic-inorganic material (Patent)

Chapter 5

Sorption and sensory activity of OIS. Perspectives of OIS utilization

5.1. Introduction

Sorption activity of synthesized hybrid organic-inorganic systems was studied. The level of adsorbed sorbate (water) was determined by the relative mass. The diffusion coefficient was calculated from the second Fick law for initial stage. The diffusion parameters of hybrid systems were compared with diffusion parameters of respective polyurethanes. The obtained results showed that sorption activity of hybrid systems are defined by the presence of hydrophilic inorganic phase, where stabilization of the incoming sorbate takes a place. Organic polymer matrix of hybrid systems does not limit the water-incoming rate and diffusion constant value depends on conditions of sorbate stabilization in the inorganic phase.

The determination of the sensory activity of hybrid systems by changing the relative resistance $R_{vapor}/R_0(\%)$ in steamy solvents vapors was done for 5 classes of solvents: aromatic hydrocarbons (toluene), oil solvents (petrol), ketones (acetone), monoatomic alcohols (ethyl alcohol) and chloride hydrocarbons (chloroform). The synthesized hybrid organic-inorganic systems showed very high sensitivity (up to 20000%) and selectivity to various solvents vapors.

5.2. Sorption activity of hybrid organic-inorganic polymer systems

The extended description and the results of investigations of sorption properties of hybrid organic-inorganic systems are represented in the attached publication (Page 118).

5.3. Sensory conductive organic-inorganic material (Patent)

The extended description and the results of investigations of sensory activity of hybrid organic-inorganic systems are represented in the attached patent (Page 130).

Sorption properties of hybrid organic-inorganic systems based on urethane oligomers and sodium silicate[6]

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Abstract

Hybrid organic-inorganic systems (OIS) based on urethane oligomers with different molecular weight and sodium silicate were synthesized. Comparing of the diffusion parameters of OIS and respective polyurethanes shows that water-absorbing properties of OIS are determined by the presence of hydrophilic inorganic phase, where stabilization of the incoming sorbate (water) takes a place. Organic polymer matrix of OIS does not limit the water-incoming rate and diffusion constant value depends on conditions of water stabilization in the inorganic phase. OIS-2102 possesses the highest sorption capacity due to the high molecular weight of respective OPG and its linear structure.

Keywords: *hybrid organic-inorganic systems, urethane oligomers, sodium silicate, in situ polymerization, sorption properties, adsorption activity.*

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1. Introduction

Polymeric compositions, which are formed by joint polymerization in liquid mixtures of reactive organic and inorganic components, are the systems with a special structure, which includes organic, inorganic polymer phases and phase of a product of interaction between organic and inorganic components [1,2]. Using an urethane oligomer as organic component, which contains free NCO-groups, gives the opportunity to obtain compositions with properties of elastomer [3]. The structure of such system is in the form of organic polymeric (polyurethane) matrix with the inorganic phase inclusions, and these inclusions have nanodimensions, namely the order 7-10 nm [4]. Such structure causes the specific electrical and diffusion properties of organic-inorganic systems (OIS), namely their relatively high conductivity, high value of dielectric constant and high sorption capacity [5]. These characteristics give the prospects for their using in the technical sphere. Thus, OIS based on polyethyleneoxyde and aluminum butoxyde synthesized in the presence of modifying additives, demonstrate high ionic conductivity, that makes possible to use them as solid electrolytes [6, 7]. The authors [3-5, 8, 9] showed that electrical, mechanical and absorption properties of OIS are determined by chemical composition of organic component.

The purpose of this work was to study the sorption properties of organic-inorganic systems based on various urethane oligomers and sodium silicate, depending on the molecular weight and functionality of the original oligooxypropyleneglycol (OPG), which was used for synthesis of urethane oligomer.

2. Experimental

OIS with polyurethane as organic component were formed by joint polymerization of urethane oligomer and sodium silicate (SS). Urethane oligomer was synthesized on 2,4-toluenediisocyanate (TDI) and oligooxypropyleneglycol (OPG) with different molecular weight and functionality equal to 2 and 3 (which determines their linear or branched structure). OPG were labeled as 1052, 2102, 3603 in accordance to their molecular weight and functionality. Besides simple polyester OPG polyester oligotetramethyleneglycol (OTMG) with molecular weight Mw = 1000, which gave a linear structure, was used. Urethane oligomers contain 3,5-5% of free NCO groups.

The length of molecular chain of urethane oligomer (molecular weight) can affect ob the properties of final products, ie to determine macrocharacteristics of OIS, in particular absorption properties. With the purpose of ascertaining the influence of molecular weight of oligomer and its degree of branching on the properties of OIS, the systems, which had as the original product of synthesis OPG-1052, OPG-2102, OPG- 3603 and OTMG-1000, have been studied. The numbers 2 and 3 are the functionality of the simple polyester OPG, ie the number of OH-groups at the sides of molecular chain. OPG with functionality 2 have a linear structure, whereas OPG with functionality 3 has a branced structure with three OH-groups at the sides of a chain. Systems based on polyester OTMG have a linear structure. Accordingly, urethane oligomers and OIS based on them have the same features. The content of inorganic phase (sodium silicate) was 20 mass % for all compositions.

In addition polyurethanes (PU) without the inorganic component were synthesized in reactions of urethane oligomers and damp air. OIS were marked according to molecular weight of OTMG and OPG as OIS-1000, OIS-1052, OIS-2102 and OIS-3603. Urethane polymers were respectively labeled as PU-1000, PU-1052, PU-2102 and PU-3603.

Samples were made in the form of disc with 30 mm in diameter and a thickness of 1 mm. Sample were submerged in distilled water for a specified period of time, then taken out. The surface was dewatered by filter paper. The sample was balanced and submerged in water for further exposition. Experiments were fulfilled at constant average temperature equal to 22 ± 2 ^{o}C.

The relative mass of adsorbed water *ΔP,%* was defined by the equation:

$$\Delta P = \frac{P - P_0}{P_0} 100$$

where P is mass of sample after exposition in water, P_0 is initial mass of dry sample.

3. Experiment results and discussion

Experimental results of water sorption in the studied systems are shown in Fig. 1 and 2. Long time isotherms (time of exposition equal to 4400 hours) of water sorption in synthesized OIS are given in Fig.1. It is obvious from the figure that all systems, except OIS-2102, reach the saturation with the relative absorbability ΔP = 30-50% during short time period, which does not exceed 300 hours. OIS-2102 has the significantly higher sorption activity with the absorbability maximum near 500% at 800 hours of exposition.

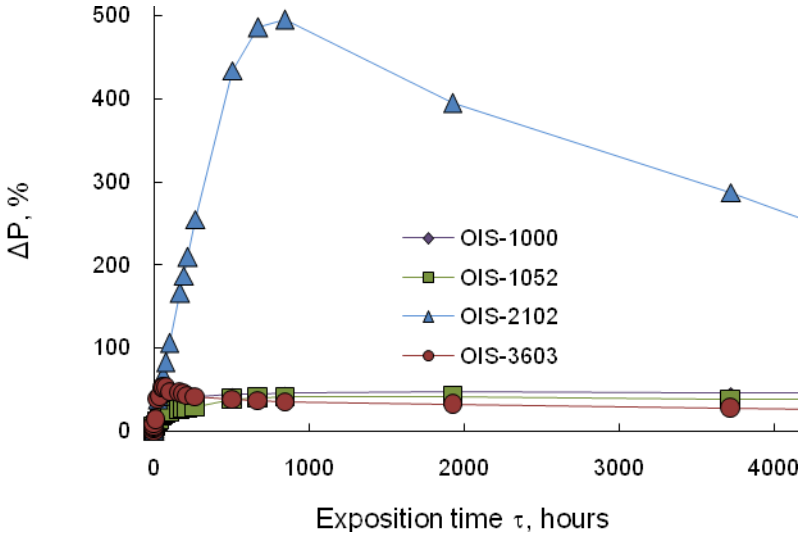

Fig. 1. Isotherms of water sorption of OIS synthesized on urethane oligomers with different molecular weight and functionality.

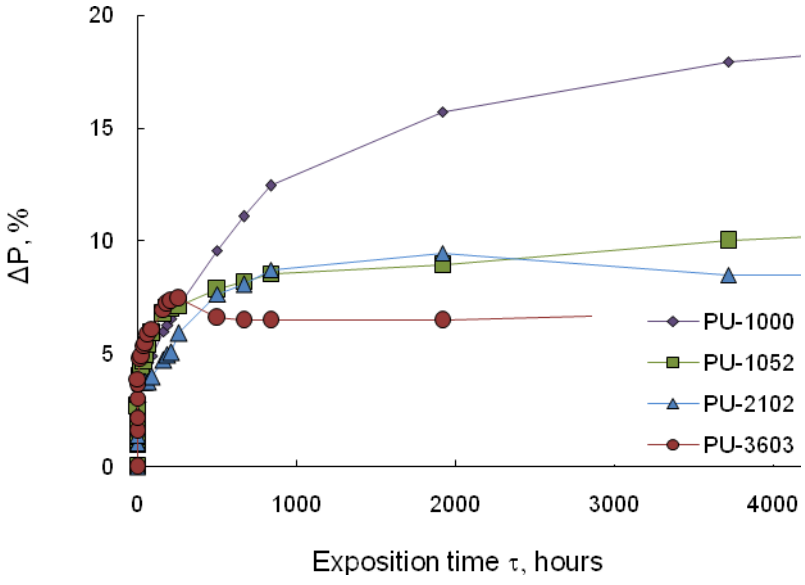

Fig. 2. Isotherms of water sorption of PU, which do not contain inorganic phase.

Sorption isotherms of polyurethanes PU significantly differ from the curves of OIS (Fig. 2). All systems, including PU-2102, drastically reach the saturation with the relative absorbability ΔP = 4-8 % during the period, which does not exceed 200 hours. The exception is the polymer system PU-1000 that has the value of relative absorbability near 20% during 4400 hours and has not yet reached the saturation, ie, this polymer is less waterproof.

The initial areas of sorption isotherms, which are represented in Fig. 3 and 4 for OIS and PU accordingly, gives the possibility to assess the rate of water diffusion in the studied compositions.

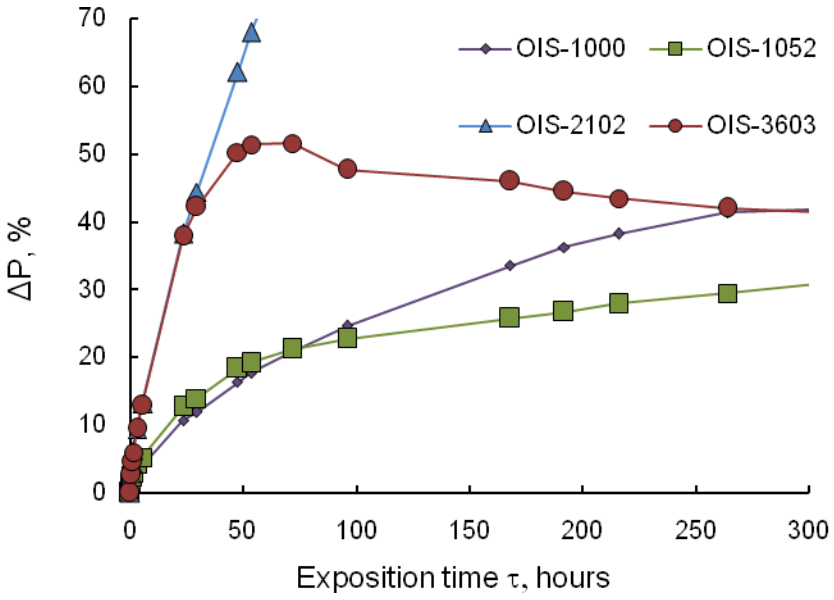

Fig. 3. The initial area of sorption isotherms of OIS-1000 – OIS-3603.

It is clear from Fig.3 that for initial exposition time in water OIS can be divided into two groups - OIS-2102 and OIS-3603, which have coincident values of relative absorbability, that are much higher than for OIS-1000 and OIS-1052, which almost coincide with each other also. OIS-3603 becomes saturated in 60 hours of exposition in water (the absorbability maximum ΔP = 51%), while OIS-2102 becomes saturated in 840 hours with ΔP = 495%.

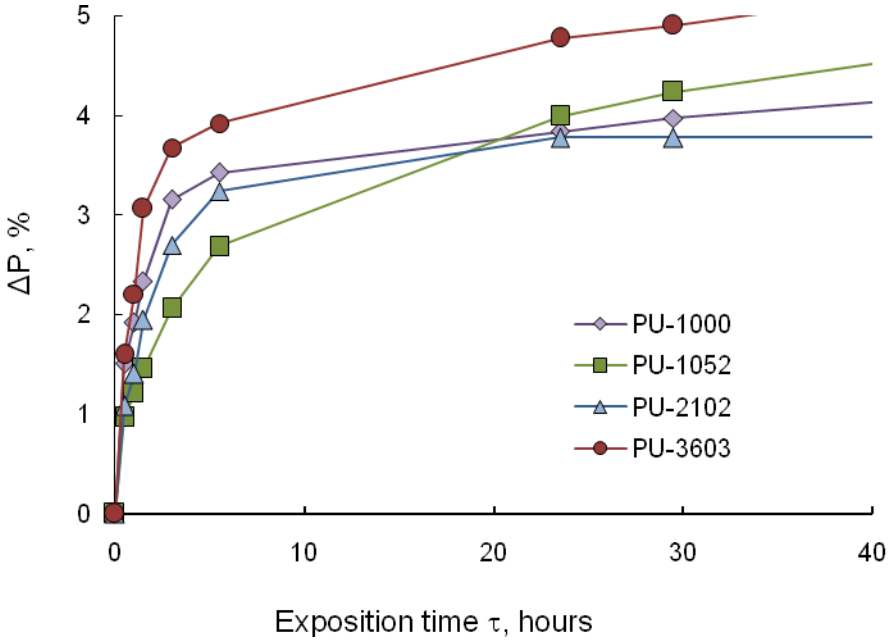

Fig. 4. The initial area of sorption isotherms of PU-1000 – PU-3603.

As regards the polymer systems (Fig. 4), the picture is somewhat different. The rapid initial period of sorption of the all studied polyurethanes takes 5,5 hours with following slow sorbate rise in polymer volume. Curves form fan-shaped dependence with the increasing of sorption rate in the series PU-1052 - PU-2102 - PU-1000 - PU-3603, thus PU-1000 does not show the anomalies of water sorption in the sorption initial area.

These results allow to calculate the diffusion coefficients of a sorbate (in our case sorbate is water or water vapors) in the studied systems, under the assumption that the sorption process follows second Fick law [10]:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial^2 x} \qquad (1)$$

where c is the concentration of sorbate, x is the distance from the edge of the sample.

This equation describes the process of change of the sorbate concentration in different points of solid material depending on time. The diffusion coefficient D is constant and characterizes the speed, with which the system can equalize concentration disparity

under known conditions. Fick's equation is valid in case of the independence of D on the concentration and with the absence of chemical reactions between sorbate and solid.

The equation (1) is used for half-infinite solid in studying of diffusion processes of the low-molecular substances in the polymer systems. In this case, the liquid diffusion is in the perpendicular direction to the solid, which belongs to the interval from $x = 0$ to $x = \infty$ and the flow of liquid from outside in the solid plane $x = 0$ occurs with constant speed. Thus, one-dimensional route of diffusion in solid is implemented. In the case, when the sample has the geometry of the thin half-infinite plate (with the thickness l) and contacts with sorbate on both sides, an analytical expression of the second Fick law can be written as [11]:

$$\frac{\Delta P}{P_{eq}} = 1 - \frac{8}{\pi^2}\sum_{k=0}^{\infty}\frac{1}{(2k+1)^2}\exp\left[\frac{-(2k+1)^2\pi^2 Dt}{l^2}\right] \qquad (2)$$

where ΔP is the sorbate mass in polymer during the diffusion time τ, P_{eq} is the equilibrium mass of the sorbate in polymer volume.

In a real experiment, when the sample has a finite size, but the thickness l is much less other dimensions, the diffusion Fick equation (2) for the initial stage can be reduced to the form [12, 13] of:

$$\frac{\Delta P}{P_{eq}} = 4\left(\frac{Dt}{\pi(2l)^2}\right)^{\frac{1}{2}} \qquad (3)$$

It follows from equation (3) that the dependence $\Delta P/P_{eq} \infty t^{1/2}$ has to be linear and the diffusion coefficient D can be calculated from the slope of this line. Fig. 5 and 6 represent initial area of sorption isotherms in coordinates of Fick equation $\Delta P/P_{eq} \infty t^{1/2}/l$. Apparently, the process of water sorption of OIS-1000, OIS-1052 and OIS-3603 follows Fick law and sorption isotherms are linear in the range of $\Delta P/P_{eq}$ values from 0 to 1. At the same time the kinetic curve of sorption is linear only in the initial area at small sorption time for the system OIS-2102, Fick law is not implemented in the whole range of $\Delta P/P_{eq}$ from 0 to 1. Therefore, in the case OIS-2102, the diffusion coefficients were calculated for small value of sorption time, where $\Delta P/P_{eq}$ reaches 0,2, and for the rest range of $\Delta P/P_{eq}$.

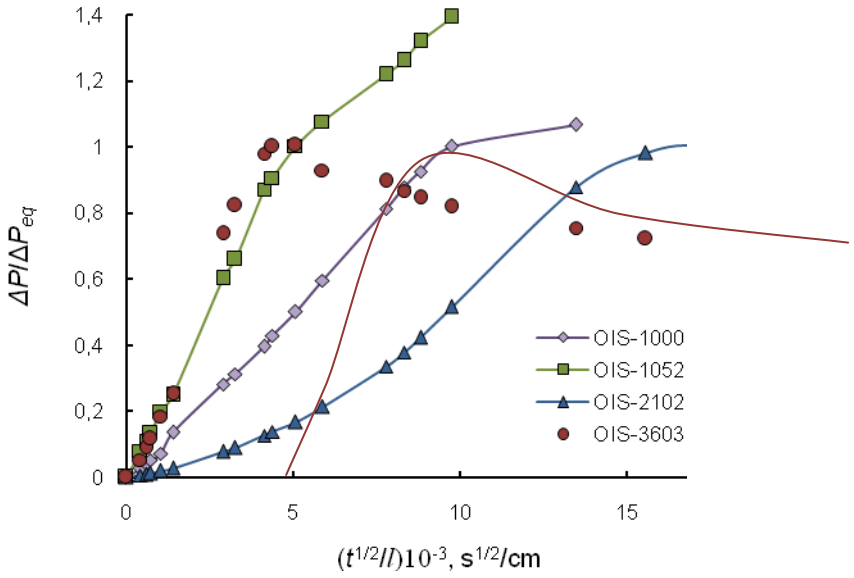

Fig. 5. The kinetic curves of sorption in coordinates of Fick equation (3) for OIS synthesized on various urethane oligomers.

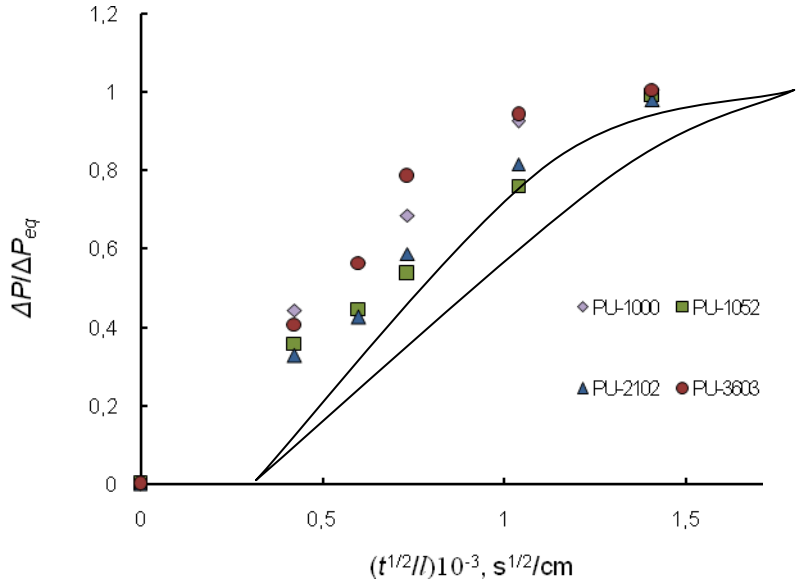

Fig. 6. The kinetic curves of sorption in coordinates of Fick equation (3) for PU synthesized on various urethane oligomers.

The values of equilibrium sorption P_{eq}, which are used for calculating the diffusion coefficient, the values of diffusion coefficient D and the values of sorption capacity P_c for the studied systems are represented in the table.

Table. Parameters of the diffusion process in OIS and PU

Compositions	ΔP_{eq}, %	τ_{eq}, hours	ΔP_c, %	D, cm^2/s	$V \cdot 10^6$, s^{-1}
OIS-1000	41,4	264	46,1	$8{,}27 \cdot 10^{-9}$	1,13
OIS-1052	21,2	71,5	38,7	$3{,}38 \cdot 10^{-8}$	1,32
OIS-2102	495	840	239	$1{,}0/3{,}1 \cdot 10^{-9}$	3,57
OIS-3603	51,4	53,5	25,4	$4{,}40 \cdot 10^{-8}$	3,57
PU-1000	3,4	5,5	18,4	$7{,}13 \cdot 10^{-7}$	2,92
PU-1052	2,7	5,5	10,3	$4{,}44 \cdot 10^{-7}$	1,91
PU-2102	3,3	5,5	8,5	$4{,}44 \cdot 10^{-7}$	2,50
PU-3603	3,9	5,5	7,2	$7{,}13 \cdot 10^{-7}$	3,41

In regard to polyurethanes synthesized on the same oligomers, the sorption process, which occurs during the short exposition time of polymers in water, follows Fick law well (Fig. 6). Diffusivity matches for PU-1000 and PU-3603 and for PU-1052 and PU-2102, and is an order of magnitude higher than for corresponding organic-inorganic systems. From a formal point of view, this is because time $t = \tau_{eq}$, at which the level of equilibrium sorption P_{eq} is reached in PU, has low value (equal to 5,5 hours), while for OIS it is an order (for OIS-2102 two orders) higher. As it is obvious from equations (2) and (3), the value of diffusion coefficient D disregards the absolute amount of sorbate Peq sorbed by solid and depends only on time τ_{eq}, when the concentration of sorbate is equalized in solid volume.

To take into account the equilibrium time of sorption and absolute amount of sorbate in system, the rate of sorption ΔV was used, which was calculated from the following equation:

$$\Delta V = \frac{\Delta P}{\Delta \tau}$$

where $\Delta\tau$ is a time calculated from the initial area of sorption isotherm.

The physical meaning of the diffusion coefficient D and rate of sorption ΔV is slightly different. The diffusion coefficient D shows how quickly the value of equilibrium sorption becomes steady in a system, i.e. how quickly the concentration of sorbate is leveled in the volume of sorbent, while the rate of sorption ΔV shows how quickly sorbate enters the material.

It is evidently from the table, that the rate of sorption ΔV rises with increasing of molecular weight of OPG, on which OIS were synthesized. The same tendency exists for the corresponding polyurethanes, except PU-1000, which has the abnormal high value of ΔV (and, respectively, the highest values P_c).

The ability of the system to accumulate a certain amount of sorbate (water in this case) can be characterized by the value of sorption capacity P_c. The value of P_c lies in the range 25,4-46,1% for all organic-inorganic systems, while for OIS-2102 it is equal to 239%. Obviously, this can be connected with the peculiarities of the structure of organic phase. The polymer part of this OIS is characterized by high elasticity (the highest among all studied systems) due to the high molecular weight of OPG and its linear structure. As a result, the hydrophilic inorganic phase freely increases its volume during process of water sorption [5]. Further, with the achievement of a certain value of elastic deformation, internal efforts, which were developed, destroy the structure of inorganic phase and amount of adsorbed water decreases. The consequence of this process is the maximum on the sorption isotherms. Obviously, these features stipulate the deviations from the Fick law (Fig. 5), because the water sorption occurs through the deformed polymer matrix. It is known that the conditions of sorption in polymers in the initial and the stressed state differ [14].

Thus, the identity of the rates of sorption ΔV and great difference of diffusion coefficients D of OIS and the corresponding PU (for OIS more than two orders of magnitude less) indicate that the diffusion process in OIS is not limited by polymer phase. It is due to the presence of hydrophilic inorganic phase and conditions of water stabilization on it, that has an effect on the values of diffusion coefficient. Low values of diffusion coefficient D testify to slow processes of water stabilization on inorganic phase. At the same time, the mechanical properties of polymer matrix (its elastic characteristics) may limit the amount of water sorbed by inorganic phase.

4. Conclusions

The comparison of diffusion parameters of organic-inorganic systems and corresponding polyurethanes demonstrates that sorption properties of OIS are determined by the presence of hydrophilic inorganic phase, on which sorbate (water in our case) is stabilized.

The rate of sorption of OIS is not limited by polymer matrix, and the value of diffusion coefficient is determined by conditions of water stabilization on inorganic phase.

OIS-2102 is characterized by the highest sorption capacity because of the high elasticity of polymer matrix due to the high molecular weight of corresponding OPG and its linear structure.

5. References

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УКРАЇНА UKRAINE

PATENT

OF THE MODEL

№ 37256

SENSORY CONDUCTIVE ORGANIC-INORGANIC MATERIAL

Given in accordance to Low of Ukraine „About copyright protection of inventions and models".

Registered in Public register of copyright of Ukraine on **25.11.2008**

Head of Department of inintellectual property — **M.V. Paladiy**

Міністерство освіти і науки України * Державний департамент інтелектуальної власності * № 1

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(54) Title of the model:

SENSORY CONDUCTIVE ORGANIC-INORGANIC MATERIAL

(57) Formula of the model:

1. The sensory conductive organic-inorganic material based on organic and inorganic components **differs by** containing urethane oligomer (UO) and isocyanate-containing modifier (IM) as organic component and poly(silicate) as inorganic component in the ratio,%:
organic isocyanate-containing component 70
inorganic component based on poly(silicate) 30.

2. According to art. 1.the proposed sensory material **differs by** containing sodium silicate as inorganic component.

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MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE

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DESCRIPTION
FOR THE PATENT OF THE MODEL

(54) SENSORY CONDUCTIVE ORGANIC-INORGANIC MATERIAL

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(22) 16.05.2008
(24) 25.11.2008
(46) 25.11.2008, Bull. № 22, 2008 p.
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(57) 1. The sensory conductive organic-inorganic material based on organic and inorganic components, **differs by** containing urethane oligomer (UO) and isocyanate-containing modifier (IM) as organic component and poly(silicate) as inorganic component in the ratio,%:
organic isocyanate-containing component 70
inorganic component based on poly(silicate) 30.
2. According to art. 1.the proposed sensory material **differs by** containing sodium silicate as inorganic component.

1 2

The material model (then model) relates to compositions based on high-molecular organic and inorganic compounds and can be used as the sensitive element of sensor devices for environment monitoring.

Known sensory conductive material which contains the polyethylene or polycarbonate, or polyamide, or polyvinylchloride as the base leaked in analine and pretreated with acid or neutral aqueous solution of oxidizing agent with the standard electrode potential in the range from 1,4 to 2,3 under the hydrogen scale. The disadvantage of the known invention is a low sensitivity to the specified range of substances [1].

The most similar by technical nature to the claimed model is the sensory conductive organic-inorganic material PPy_yMoO_3 based on polypyrole as the organic component and molybdenum oxide as the inorganic component [2]. The value of material sensitivity to vapors of different solvent classes lies in the ranges from 0,1 to 6% relative to initial values of resistivity. The material has superior physical-mechanical properties (improved elasticity) and high chemical purity due to removal of residual aniline and oxidation products. Disadvantages of this sensory material are:

- low sensitivity to solvent vapors;
- long-time response on solvents vapors.

The tasks of the model is to improve the sensory conductive material, in which the sensitivity to solvent vapors increases and the response to solvent vapors effect decreases due to matched compositions and components ratio.

The task is achieved by using sensory conductive organic-inorganic materials based on reactive organic and inorganic components, which, in accordance with the model, contains urethane oligomer (UO) and isocyanate-containing modifier (IM) as organic component and poly(silicate) (PS) as inorganic component in the ratio,%:

- organic isocyanate-containing component - 70;
- inorganic component - 30.

The ration between UO and IM is taken from 46%/24% to 0%/70%. The sensory conductive organic-inorganic material contains sodium silicate as inorganic component. The conductivity of proposed sensory organic-inorganic material depends on the content of free NCO-reactive groups in the organic component. The content of NCO-groups is from 13 to 32% depending on UO/IM ratio.

Urethane oligomer with molecular weight Mw = 4500 was synthesized on 2,4-toluenediisocyanate and oligooxypropyleneglycol with molecular weight Mw = 2100.

Isocyanate-containing modifier contains free NCO-groups which react with the inorganic component.

Used sodium silicate has such characteristics: silicate modulus is 2,8, density is 1.45 g/cm^3.

The composition and compounds ratio of organic component in the proposed sensory material listed in the **table**.

The sensory conductive organic-inorganic polymer material is obtained as follows:

Example 1. Urethane oligomer is mixed with isocyanate-containing modifier in the ratio according to the table within 5 minutes. The inorganic component (sodium silicate) is added into obtained mixture of organic compounds, which represents organic component and is being mixed for 5 minutes. The ratio between the organic component (UO + IM) and the inorganic component PS is taken 70/30 for all compositions. The thin layer with the thickness equal to 50 microns of the reactive mixture obtained, which is light yellow color viscous liquid, is applied on the metal electrodes. Electrodes is in the form of interpenetrating combs with the distance between the contacts equal to 25 microns. The number is 25 for each electrode and equal for both electrodes.

The curing of the material runs duringr 24 hours at temperature 25 ± 1 ^{o}C and humidity 45%.

Recent examples tabulated.

The resistance **R** of the sensory material was measured under the voltage equal to 100 V in air atmosphere with humidity 45% at temperature 25 ± 1 ^{o}C ($\mathbf{R_0}$) and near the surface of the solvent in the closed volume with saturated solvent vapor ($\mathbf{R_{vapor}}$). The measurements were fulfilled as follows: the electrodes with the proposed sensory conductive organic-inorganic material were placed in the closed volume with steamy solvent vapors suring 300 seconds and the relative change of resistance

$\mathbf{R_{vapor}/R_0(\%)}$ was measured then removed and dried to the original state during 300 seconds. The cycle was repeated 3 times.

The determination of the sensory material sensitivity by changing the relative resistance $\mathbf{R_{vapor}/R_0(\%)}$ in steamy solvents vapors was done for 5 classes of solvents: aromatic hydrocarbons (toluene), oil solvents (petrol), ketones (acetone), monoatomic alcohols (ethyl alcohol) and chloride hydrocarbons (chloroform).

The sensory materials obtained with different compounds ratio in organic component, the sensitivity value of the proposed sensory material and the names and classes of solvents are listed in the **table**.

It follows from the table that the proposed material with different compounds ratio in organic component has a significantly higher sensitivity to solvents vapors and shorter response time compared to analog.

Sensitivityof the proposed material to solvents vapors lies in the range from 0 to 20300%, while this value lies between 0 and 2,0% for the prototype.

The response time to solvents vapors reduced by half (300 seconds) for the proposed material compared with the prototype (600 seconds).

The table analysis shows that composition 2 is the most sensitive to the toluene vapors (aromatic hydrocarbons) with value $\mathbf{R_{vapor}/R_0}$ = 80% vs. the prototype with value $\mathbf{R_{vapor}/R_0}$ <0,1%. The composition 3is the most sensitive to the petrol vapors (oil solvents) with value $\mathbf{R_{vapor}/R_0}$ = 40% vs. the prototype with value $\mathbf{R_{vapor}/R_0}$ <0,1%. The composition 1 is most sensitive to the acetone vapors (ketones) with value $\mathbf{R_{vapor}/R_0}$ = 1190 % vs. the prototype with value $\mathbf{R_{vapor}/R_0}$ = 0,2%. The composition 4 is the most sensitive to the vapors of ethyl alcohol (monoatomic alcohols) with value $\mathbf{R_{vapor}/R_0}$ = 20300% vs. the prototype with value $\mathbf{R_{vapor}/R_0}$= 0,7%. The composition 2 is the most sensitive to the chloroform vapors (chloride hydrocarbons) with value $\mathbf{R_{vapor}/R_0}$ = 1400% vs. the prototype with value $\mathbf{R_{vapor}/R_0}$ = 2%.

Compositions of the sensory material			**Names and classes of solvents** Value of sensitivity determined by changing the relative resistance $\mathbf{R_{vapor}/R_0(\%)}$					
№	Components of sensory material	Ratio UO/IM/PS	**Toluene** Aromatic hydro carbons	**Petrol** Oil solvents	**Acetone** Ketones	**Ethyl alcohol** Monoatomic alcohols	**Chloroform** Chloride hydrocarbons	**Response time,** s
1	UO IM PS	**46 %** **24 %** **30%**	50	20	1190	400	780	300
2	UO IM PS	**35 %** **35 %** **30%**	80	30	300	2530	1400	300
3	UO IM PS	**14 %** **56 %** **30%**	<0,1	40	100	16400	110	300
4	UO IM PS	**0 %** **70 %** **30%**	<0,1	30	<0,2	20300	<2,0	300
5	Prototype: sensory material PPy_yMoO_3		<0,1	<0,1	0,2	0,7	2,0	600

Sources of information.
1) Patent (11) 75761 (19) UA, № 20040604577, 15.05.2006.

2) European patent application (11) EP 1457772 A2, (19) European patent office, № 04075840.1, 12.03.2004

ABSTRACT

for the patent of the model

MPK7 S08L 75/04 C08K 3 / 34 G01N 27/12

(54) Sensory conductive organic-inorganic material

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The material model relates to compositions based on high-molecular organic and inorganic compounds and can be used as the sensitive element of sensor devices for environment monitoring.

The task of the model is to improve the sensory conductive material, in which the sensitivity to solvent vapors increases and the response to solvent vapors effect decreases due to matched compositions and components ratio.

In accordance to the model, the proposed sensory conductive organo-inorganic material based on reactive organic and inorganic components contains urethane oligomer (UO) and isocyanate-containing modifier (IM) as organic component and poly(silicate) as inorganic component in the ratio of organic and inorganic components 70/30. The ratio between UO and IM is taken from 46/24 to 0% / 70%.

High values of sensitivity to different classes of solvent vapors, rapid response to solvents vapors effect is achieved by using organic-inorganic material synthesized in reactive mixture of organic and inorganic components.

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Conclusions

The extended conclusions were represented in the attached publications. The major conclusions can be classified as follows:

- It was shown that two hybrid organic-inorganic networks MDI/SS and PIC/SS are formed in the structure of OIS. The ratio MDI/PIC determines the content of NCO-groups in the reactive mixture and, accordingly, controls the contribution of each network in the structure of OIS that enables to regulate directly electrophysical properties of OIS. A spatial structural model that describes the structural organization of OIS depending on the composition of organic component was developed.
- For the first time it was revealed that for the systems studied the concentration dependences of rheokinetic parameters had abnormal extreme character associated with complex interactions of organic and inorganic components during the polymerization reactions.
- Mechanical and thermomechanical properties of hybrid systems are defined by the conditions of their structure formation and depend on the type of dominant network (MDI/SS or PIC/SS) in the bulk of OIS. In the case of the dominant network MDI/SS hybrid system is characterized by high deformative properties, low thermal stability and high-value time of mechanical relaxation. In the case of the dominant network PIC/SS compositions have high rigidity, heat resistance and high values of Young modulus.
- First it was established that the conductivity process of OIS included three mechanisms of charge transport: proton conductivity ($\sigma_{DC}\approx10^{-9}$ S/cm that is ensured by the presence of protons H^+), ionic conductivity ($\sigma_{DC}\approx10^{-11}$ S/cm, associated with the presence of sodium ions Na^+) and conductivity of organic matrix ($\sigma_{DC}\approx10^{-15}$ S/cm). It was defined that the hybrid network MDI/SS is characterized by the presence of all types of conductivity, while the conductivity of organic matrix is prevailing in the hybrid network PIC/SS. The conductivity model of OIS was proposed.

- For the first time it was shown the presence of high sensitivity and selectivity of OIS to vapors of different types of solvents (sensitivity by ratios I/I_0 and σ_{AC}/σ_{0AC} is up to 10^3, sensitivity by ratio $\varepsilon/\varepsilon_0$ is up to 10^4) depending on the composition of OIS and the chemical nature of solvent.

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Publications

1. ***The Anomalous Behavior of Physical-Chemical Parameters During Polymerization of Organic-Inorganic Polymer Systems Based on Reactive Oligomers***
   M. Iurzhenko, Ye. Mamunya, G. Boiteux, G. Seytre, E. Lebedev
   Printed in Rep. of NASU 9 (2008) 81-84.
   Submitted to e-polymer J.

2. ***Mechanical Properties of Organic-Inorganic Polymer Systemsbased on Urethane Oligomers***
   Ye.P. Mamunya, M.V. Iurzhenko, E.V. Lebedev, V.V. Davydenko, G. Boiteux, G. Seytre
   Printed in Ukr. Polym. J. 31 (2009) 51-57.
   Submitted to J. of Non-Cryst. Sol.

3. ***Thermomechanical and Electrical Properties af Hybrid Organic-Inorganic Polymer Systems Based on Isocyanate-Containing Oligomers***
   Ye.P. Mamunya, M.V. Iurzhenko, E.V. Lebedev, S.S. Ishchenko
   Printed in Ukr. Polym. J. 29 (2007) 100-105.

4. ***Dielectric and Thermal-Mechanical Properties of Hybrid Organic-Inorganic Polymer Systems Based on Isocyanate-Containing Oligomers***
   Ye.P. Mamunya, M.V. Iurzhenko, E.V. Lebedev, S.S. Ischenko, G. Boiteux, G. Seytre
   Printed in J. of Non-Cryst. Sol. 353 (2007) 4288-4292.

5. ***Relaxation Processes in Hybrid Organic-Inorganic Polymer Systems Polymerized In Situ.***
   M.V. Iurzhenko, Ye.P. Mamunya, G. Boiteux, G. Seytre, E. Nikaj, O. Gain, E.V. Lebedev, S.S. Ischenko
   Submitted to Europ. Polym. J.

6. *Sorption Properties of Hybrid Organic-Inorganic Systems Based on Urethane Oligomers and Sodium Silicate*

   Ye.P. Mamunya, M.V. Iurzhenko, E.V. Lebedev, S.S. Ishchenko, I.M. Parashchenko

   Printed in Ukr. Polym. J. 30 (2008) 37-42.

   Submitted to polymer J.